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BSI British Standards

Guide to on-site test methods for the analysis of waters

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Foreword

Publishing information

This British Standard BS 1427 is published by BSI and came into effect on 1 January 2009. It was prepared by Subcommittee EH/3/2, *Physical, chemical and biochemical methods*, on behalf of Technical Committee EH/3, *Water quality*. A list of organizations represented on the committee can be obtained on request to its secretary.

Supersession

This standard supersedes BS 1427:1993, which is withdrawn.

Information about this document

This guide describes methods for the analysis of industrial and other waters which can be undertaken outside of the chemical laboratory, as on-site tests, when the purpose of the test is to characterize the water under test for either quality or process control purposes. With some determinands, which can be unstable after sampling and which cannot be stabilized, on-site tests provide a suitable means of obtaining fit-for-purpose test results. The test methods described in this Standard comprise simple procedures for use either by a trained analyst, or following appropriate training, by a suitable individual. Since 1993, many industrial laboratories have been shut down and the use of on-site methods increased significantly. A very significant proportion of these tests are carried out by non-analysts using proprietary test-kits.

This British Standard is not intended as a substitute for, or alternative to, other British Standards on the quantitative analysis of waters, namely BS 6068 (all parts) and BS 2690, which remain the reference methods for use in a laboratory. The methods described in this British Standard are mostly based on principles and/or procedures used in BS 6068 and BS 2690 and their associated updates.

This revision of BS 1427 contains updates to specific methods since the previous standard and provides guidance on the use of the much wider range of available commercial test-kits and test-kit equipment since the 1993 previous version of this standard. Since 1993, the range, type and quality of commercial test-kits/apparatus have improved considerably, producing significant benefits in terms of increased reliability and ease of use for on site testing. The use of pre-packaged chemicals and reagents has also reduced health and safety risks associated with handling chemicals and enhanced the simplicity of testing.

The layout of this British Standard has been significantly amended since the 1993 version to reflect the very much greater availability of commercial test-kits and the continuing need for effective quality control procedures, both of which feature in extended annexes.

Traditional colorimetric, titrimetric and instrumental methods for water analysis are still shown in this standard. The test procedures for the colorimetric and instrumental test methods are specific to the colour comparator or instrument described. The test procedures for each commercial test-kit method are specific to the parameter described. The detailed test procedure defined/described by the manufacturer are to be followed when the manufacturer's test-kit is used.

A standardized approach to describing tests undertaken with the colour comparator method is shown separately in Annex B.

Commercial test-kit methods available are shown in Annexes I, J and K.

As a guide, this British Standard takes the form of guidance with a number of informative annexes. The full set is:

- Annex A, *Guidance on training, supervision and associated needs*
- Annex B, *Example of a documented test-kit method and associated sampling protocol for a colorimetric method*
- Annex C, *Typical expected result confidence intervals from a given QC solution from a range of test-kits from two manufacturers*
- Annex D, *An example of target test-kit requirements for a COD test-kit used in a designated room/area testing facility*
- Annex E, *An example of target test-kit requirements for a free and total chlorine test-kit used on-site at the sampling location*
- Annex F, *An example of routine QA/QC documentation for a COD test*
- Annex G, *An example of routine QA/QC documentation for a free and total chlorine test*
- Annex H, *Example of Shewart control charts*
- Annex I, *Test-kit method overview*
- Annex J, *Summary of test-kits*
- Annex K, *Availability of visual test sticks*

Use of this document

As a guide, this British Standard should not be quoted as if it were a specification, and particular care should be taken by manufacturers and users to ensure that claims of compliance are not misleading or taken out of context. Any user claiming compliance with this British Standard is expected to be able to justify any course of action that deviates from its recommendations. Any compliance claim should be supported with appropriate validation data.

Users cannot specify the on-site test performance required and how to monitor that this performance is met on an on-going basis. They can then either devise an on-site method or find a test-kit that can meet this specification for all relevant matrices. It is felt that the vast majority of users of this standard will adopt the latter option. This document aims to provide guidance on how to do this, but the user needs to decide the level of performance required to ensure that all results are fit for the intended purpose. Users in this context include the end user of the results and the organization carrying out the test.

It is not possible to cite or describe specific individual commercial water test-kits in a British Standard for commercial impartiality reasons. In Annex H, a general overview of the major commercial water test-kits currently available is given.

The water test-kit market is fast moving and extremely innovative. Users of test-kits are strongly advised to regularly check the availability of improved test-kits meeting their requirements. Most relevant information is available on the various test-kit manufacturers' websites and can be readily assessed via a search engine. It is important to appreciate that much of this performance data is best-case data, often related to aqueous standards. Users always have to assess any new proposed test-kit that they intend to use against all relevant sample matrices that are to be tested.

Notice has been taken of the proposed MCERTS *Performance Standards and Test Procedures for Water Test-kits* in the writing of this standard.

Hazard warnings

WARNING. This British Standard calls for the use of substances and/or procedures that can be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage.

Presentational conventions

The provisions in this standard are presented in roman (i.e. upright) type. Its recommendations are expressed in sentences in which the principal auxiliary verb is "should".

Commentary, explanation and general informative material is presented in smaller italic type, and does not constitute a normative element.

The word "should" is used to express recommendations of this standard. The word "may" is used in the text to express permissibility, e.g. as an alternative to the primary recommendation of the clause. The word "can" is used to express possibility, e.g. a consequence of an action or an event.

Notes and commentaries are provided throughout the text of this standard. Notes give references and additional information that are important but do not form part of the recommendations. Commentaries give background information.

Contractual and legal considerations

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard cannot confer immunity from legal obligations.

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Section 1: General

1.1 Scope

*COMMENTARY ON **1.1**. Emergency screening analysis for major pollution incidents is not covered. Information on this is available via the US EPA which has set up an Environmental Technology Verification (ETV) Programme [1] and published a series of verification reports developed for each verified technology. The reports contain the performance verification test results and meet the ETV programme's stringent quality assurance and peer review requirements for a wide range of advanced monitoring systems for water analysis mainly directed to emergency incidents. Further information on rapid analytical response issues in emergency situations is available (Thompson and O'Neill, 2006 [2] and Thompson, 2009 [3]).*

This British Standard describes information and guidance on test methods for the analysis of industrial and other waters which are applicable outside of a conventional laboratory as either in situ on-site tests; or the use of a close suitable designated room/area testing facility. For some tests this could include dedicated space in a designated vehicle or caravan. These test methods can relate to compliance, water quality and process control purposes. No recommendation is given as to which test is applicable to a particular type of water, nor is it implied that in any given case all tests or any particular suite of tests are necessary. The selection of tests depends on local requirements and conditions. Samples requiring preservation for subsequent analysis are outside of the scope of this British Standard.

Certain tests such as adsorbable organic halides (AOX), chemical oxygen demand (COD), total organic carbon (TOC) and total nitrogen need a suitable designated test room/area facility and are not considered suitable for testing outside of these designated areas.

Sample stability is not considered to be a significant problem as most test-kit measurements are carried out with minimal delay.

Most of the methods described in this standard can be applicable for use on clean or lightly polluted waters which might have undergone treatment or been modified for industrial use. Typically, the types of waters for which the tests are intended include the following:

a) boiler waters;

b) cooling waters;

c) waters from hot water systems;

d) waters from air conditioning systems;

e) waters from industrial air washing systems;

f) potable waters;

g) ground waters;

h) surface waters;

i) process waters; and

j) swimming pool waters.

Certain more heavily polluted waters can be routinely tested for certain control purposes for specific determinands using the test methods cited in this British Standard. Such waters include:

1) sewage works influents and effluents;

2) selected industrial effluents.

Emergency screening analysis for major pollution incidents is not covered (see commentary).

The on-site methods outlined in this British Standard include titrimetric, colorimetric and instrumental analytical techniques and also includes consideration of commercial test-kits: their general principles and formats available. It is generally accepted that in the UK, the vast majority of on-site measurements are carried out using commercial test-kits rather than user-devised test-kit type methods

following similar equivalent method procedures to those used in conventional laboratories. Also the designated room/area testing facility titrimetric methods described in Section **4** of this standard might require staff with a greater degree of training than commercial test-kit titrimetric methods which can be readily used outside of these areas. These methods are less likely to be used by non-analysts than the more robust test-kit titrimetric methods.

The technique used and principle of the designated room/area testing facility titrimetric method are described within each test method and each method is self-contained within a standard format.

This British Standard does not apply to radioactivity, ecotoxicity (See Persoone et al., 2000 [4]) or microbiological testing. Spot tests are not covered (Jungris, 1997 [5]).

Many of the relevant methods are suitable for analysis for the water framework directive (see Note and SWIFT 2003 [6]), water for human consumption (see Note) and for monitoring of discharges to water and sewer (EA, 2006 [7] and Dixon and Gardner, 1997 [8]).

NOTE EC 2000 [9] is known as 'the water framework directive; EC 1998 [10], The Water Supply (Water Quality) Regulations 2000 [11] and DWI [12] relate to water for human consumption.

1.2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

BS 1704:1985/ISO 1770:1981*, Specification for solid-stem general purpose thermometers*

BS 2586*, Specification for glass and reference electrodes for the measurement of pH*

BS EN ISO 3696:1995*, Water for analytical laboratory use – Specification and test methods*

1.3 Terms and definitions

For the purposes of this British Standard, the following terms and definitions apply.

1.3.1 on-site tests
quantitative chemical and physical tests undertaken in situ on a site, or within a designated room/area testing facility, to enable water quality assessments to be undertaken

NOTE Some on-site tests do require a designated room/area testing facility and these tests are clearly indicated in this standard (See Annex I).

1.3.2 designated room/area testing facility
basic laboratory facilities in a designated room (or a designated secure area in a room)

NOTE 1 This could include provision of electricity, fixed bench facilities, water supply and suitable drainage; analytical balance, heating block, fume extraction, etc. Other uses of the room or area have to be controlled

so as not to interfere in any way with the analysis. This ought to include controlled access and restricted activities compatible with use as a test area. For some tests this could include dedicated space in a designated vehicle or caravan.

*NOTE 2 It would appear that the majority of on-site (**1.3.1**) tests are carried out in a designated room/area testing facility.*

1.3.3 designated test room/area test
test that requires a designated room/area testing facility (**1.3.2**)

*NOTE This could include provision of electricity, fixed bench facilities, water supply and suitable drainage; analytical balance, heating block, fume extraction, etc. (See also **1.3.2**).*

1.3.4 ready to use test-kit
commercially packaged complete analytical system in a portable kit format designed for on-site testing

NOTE 1 Some test-kits can only be applied in designated test rooms/ areas and laboratories.

NOTE 2 Test-kits are intended as simplified, easy-to-use tests for analysis of water quality, usually within specified concentration ranges and designated sample matrices.

1.3.5 precision
random error expressed as the standard deviation (within a batch and between batches) of the spread of results about the mean

1.3.6 trueness (the systematic error)
difference between the mean value of the large number of repeated measurements and the true value

1.3.7 bias
synonym of trueness (**1.3.6**)

1.3.8 uncertainty
parameter associated with the results of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand

NOTE It therefore takes account of all the significant sources of variability in the measurement results and should include the effect of both random and systematic errors. No part of uncertainty can be corrected for.

1.3.9 confidence interval
CI
interval estimate of a population parameter; instead of estimating the parameter by a single value, an interval of likely estimates is given

NOTE Most confidence intervals are stated at the 95% level.

1.3.10 accuracy
closeness of agreement between a test result and the accepted reference value

NOTE Definition from BS ISO 5725-1:1994.

1.3.11 method validation
confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled

NOTE Definition from BS EN ISO IEC 17025.

1.3.12 system suitability checks
SSC
simple tests to ensure that the associated test-kit instrumentation is functioning within specified limits before commencing analysis

1.3.13 quality assurance
part of quality management focussed on providing confidence that quality requirements will be fulfilled

1.3.14 quality control
part of quality management focussed on fulfilling quality requirements

1.3.15 repeatability
precision under repeatability conditions. i.e. conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time

1.3.16 reproducibility
precision under reproducible conditions, i.e. conditions where independent test results are obtained with the same method on identical test items in different laboratories by different operators using different equipment

1.3.17 limit of detection
lowest concentration of an analyte that can be detected with a specified degree of statistical certainty

1.3.18 proficiency testing
assessment of laboratory testing performance by means of interlaboratory comparison by distributing common samples to a number of different laboratories

1.3.19 control charts
routine plotting of analysis data obtained from the analysis of quality control materials to check if the results lie within pre-determined limits

1.3.20 target value chart
control chart with fixed rather than statistically derived limits

1.3.21 internal AQC
analysis of known samples or standards carried out with each batch of analysis

1.3.22 recovery
fraction of the amount of analyte added which is found using the method

NOTE If a known amount of an analyte is added to an aliquot of a test sample and the amended and unamended samples are analysed, then the recovery is the fraction of the amount of analyte added which is found using the method.

1.3.23 fitness for purpose
process of assessing that a method is suitable for a given application

1.3.24 instrumental method
method that employs non-photometric instrumentation that can be used for in situ on-site measurements

NOTE It can also be used in a designated room/area testing facility analysis.

1.3.25 standard addition
method of standard addition used in instrumental analysis to determine the concentration of a substance (analyte) in an unknown sample by comparison to a set of the test sample solutions with increasing additions of known concentration of the analyte

NOTE This is similar to using a calibration curve. The aim is to at least double the concentration of the analyte with the largest addition. Standard addition can be applied to most analytical techniques and can be used instead of a conventional calibration graph to minimize the matrix effects.

1.3.26 analyte
chemical or constituent being determined

1.3.27 carryover
contamination of a subsequent sample by a previous sample, typically due to incomplete cleaning of a reused test-kit component

1.3.28 interference
effect of a matrix component that might cause an analytical bias or that might prevent a successful analysis

1.3.29 matrix
sample contents other than the target analyte

1.3.30 in situ
within, or directly adjacent to, the water space

1.3.31 on-site
method that can be carried out at a location close to where the sample is taken

NOTE Generally, fixed facilities or services might not be available.

1.4 Information on MCERTS performance standards and test procedures for water test-kits

The Environment Agency (EA) established its Monitoring Certification Scheme (MCERTS) to deliver quality environmental measurements in 1997 and a number of performance standards have been developed for air, land and water (see www.mcerts.net).

The Environment Agency MCERTS scheme includes *Performance Standards and Test Procedures for Portable Water Monitoring Equipment* [13]. It provides a certification framework for instruments designed for use in the field and applies to any technology. It describes laboratory and field tests to assess the operation of sensors for the measurement of: dissolved oxygen; conductivity; pH; turbidity; temperature; ammonia; nitrate; nitrite; orthophosphate; and chlorophyll-a. Other parameters may be covered in future, if there is sufficient industry interest and support.

The *Performance Standards and Test Procedures for Portable Water Monitoring Equipment* [13] standard covers equipment used for monitoring of:

- waste water treatment;
- rivers, lakes and estuarine environments;
- water storage reservoirs;

- boreholes and groundwater;
- trade effluents.

A portable water monitor (PWM) comprises of all components required to make the measurement. This may include reagents, devices required for sample preparation and any sample delivery system. A PWM should provide a direct read-out of the determinand, in appropriate units of measurement and not require reference to a calibration chart or table. Relevant water test-kits can also be submitted for accreditation under this scheme.

The Environment Agency is in the process of considering the development of a separate MCERTS standard specifically for water test-kits.

Test-kit manufacturers can receive an MCERTS certificate for a given test-kit with a five year expiry date, if they demonstrate that they can meet the relevant MCERTS requirements.

Expected advantages of MCERTS for test-kits are:

- makes available a certification scheme that is formally recognized within the UK and is acceptable internationally;
- gives confidence to regulatory authorities that test-kits/ instrumentation, once certified, are fit-for-purpose and capable of producing results of the required quality and reliability;
- gives confidence to users that the test-kits/instrumentation selected are robust and conform to performance standards that are accepted by the Environment Agency;
- supports the supply of accurate and reliable data to the public;
- provides test-kit manufacturers with an independent authoritative endorsement of their products, which will facilitate their access to international markets and increase the take-up of their products in the UK.

Product certification comprises three phases. These are as follows.

- Laboratory testing – used to determine performance characteristics, where such testing requires a highly controlled environment.
- On-site or designated test room/area testing, carried out on waters that are representative of the intended applications.
- Surveillance (initial and continuing), which comprises an audit of the manufacturing process to confirm that the manufacturer has provisions to ensure manufacturing reproducibility and to control any design changes to ensure that they do not degrade performance below the MCERTS standards.

Users of this British Standard are advised that, where there are any MCERTS services and equipment available relevant to the analysis being performed, users should consider the desirability of using these.

Section 2: Physical and chemical test methods: general information

2.1 Health and safety

2.1.1 General

The test methods described in this British Standard should be undertaken only after suitable training has been received (see **2.2**). Where necessary, adequate supervision in undertaking the tests should be provided. Training and associated documentation in areas such as safe working practices should also be provided which should pay due regard to all potential hazards of on-site operations.

NOTE 1 Attention is drawn to the Health and Safety at Work etc. Act 1974 (HSE, 1974) [14] and the need for management and test operators to make adequate provisions for safe working.

The test operator should be fully trained with respect to and always following safe working procedures.

NOTE 2 Attention is drawn to the Control of Substances Hazardous to Health Regulations 2002 (COSHH, 2002) [15] which mention risk assessment being undertaken and appropriate safety measures to be implemented when using potentially hazardous chemicals.

NOTE 3 The chemicals referred to in this British Standard are typical of chemicals used in a laboratory environment and hazard data sheets are obtainable from chemical suppliers. Commercial test-kits might also incorporate hazardous chemicals and manufacturers ought to provide warning notices and relevant hazard data sheet(s) with the kits.

This British Standard does not define safe working procedures for test methods or commercial test-kits; in addition to laboratory and site work safety training, the check-lists in **2.1.2** to **2.1.3** for working practices should be considered, as they include some general safeguards against potential hazards within routine control testing.

2.1.2 Personal safety precautions

Personal safety precautions that should be followed include the following.

a) Where appropriate, protective safety glasses should be worn when following test methods or when handling hazardous chemicals. An emergency eyewash bottle or facility should be made available.

b) Hand washing facilities should be provided whilst working on-site and/or in a designated test room/area.

c) Where appropriate, suitable protective clothing when sampling, testing or when handling hazardous chemicals should be worn.

d) Hand-to-mouth actions, such as smoking, drinking or eating should not be undertaken whilst testing or handling hazardous chemicals. Cosmetics or handcreams, etc. should not be applied.

e) The use of self-adhesive labels should be encouraged.

f) Solutions should never be pipetted by mouth.

g) Because of potential microbiological contamination in water samples, samples should always be taken in bottles with secure caps and the hands washed after sampling or carrying out tests. The hands should also be washed before leaving a site location.

h) Lone worker implications at unmanned sites should be considered.

2.1.3 Care in the work zone (i.e. on-site or in designated room/area testing facilities)

Work zone precautions that should be followed include the following.

a) Designated room/area testing facilities should be kept clean and tidy.

b) The test-kit user should ensure that chemicals and test-kits are stored safely using clear, unambiguous labelling. A regularly updated register of all chemicals and test-kits stored should be kept by a suitable nominated appropriate person.

c) All spillages should be cleaned up immediately in a safe manner.

d) Hazardous chemicals are usually sold in protective packaging clearly marked with appropriate hazard warnings; the chemicals should be stored securely and safely as directed on the label or material data safety sheet supplied with the chemical. Preparation of test reagents should be restricted to suitably trained staff unless the test operative is given suitable training and detailed instructions on preparation procedures.

2.1.4 General safeguards

General safegurards that should be implemented include the following.

a) Safe working procedures for the designated room/area testing facility and when working on-site should always be followed.

b) Damaged equipment or broken or chipped glassware should not be used.

c) Test operatives and samplers should be trained and checked/audited in safe working procedures for testing.

d) Where chemicals are transported for on-site testing, suitable protective containment should be identified and used.

e) Documented instructions should be provided (and always followed by test operatives) for the safe disposal of any waste material.

2.2 Training, supervision and associated needs

Satisfactory training is essential to safeguard the test operator and to achieve acceptable test results. This British Standard does not define the training or criteria required for training, but Annex B gives some guidance on training, supervision and associated needs.

Training should be subject to objective assessment against preset criteria by a competent person: the final approval of the test operative lies with the trainer. It is essential that the test-kit user is fully trained to use the test-kit to give fit-for-purpose results and that this training is maintained.

2.3 Test facilities

Test results can have a significant random error associated with the physical and environmental conditions under which the test is carried out. There are only limited measures that can be implemented to improve the environment when carrying out open site in situ testing, but provision of a fit-for-purpose designated room/area testing facility within a fixed enclosed site can improve the quality of testing. This area should, ideally, be controlled-access, only subject to activities which are compatible with use as a testing area and ideally provide the following features:

a) adequate environmental conditions, including provision of lighting and heating;

b) services including power outlets, running water and drainage and a supply of RO/DI water to BS EN ISO 3696:1995, Grade 3;

c) bench top working space and secure cupboard storage space for chemicals and apparatus;

d) for health and safety reasons, access should be restricted and the designated testing room/area made secure when not in use; other uses of the room or area should be controlled so as not to interfere in any way with the analysis; and

e) for any tests using significant amounts of hazardous reagents and/or involve complex procedures (e.g. AOX, COD, TOC and total Nitrogen) a designated room/area testing facility is essential.

The vast majority of test-kit measurements are carried out in designated room/area testing facilities.

2.4 Sampling, sampling preservation and sample pre-treatment considerations

NOTE 1 Some instrumental test methods can be applied in situ by direct immersion of measuring electrodes into the body of water, which obviates the need for sampling (e.g. DO; redox potential; pH and electrical conductivity). This assumes that it has been shown to be safe to carry out such measurements.

Where it is necessary to obtain a sample from a liquid stream, it is essential to obtain a representative sample, which should be tested as quickly as possible to retain sample integrity. Correct sampling procedures and, if relevant, the appropriate sample preservation and pre-treatment techniques are essential for fit-for-purpose analytical results. Sample preservation is seldom required for on-site measurements which are normally carried out within a few minutes of sampling. Guidance on sampling is available from a number of sources (see Note 2). Comprehensive details of sample preservation are given in BS EN ISO 5667-3.

NOTE 2 Further details on sampling and sample preservation are described in BS 6068-6.7, BS 3285, BS 6068-6 and BS EN ISO 5667-3.

NOTE 3 If the test-kit is used for field screening to indicate the need for samples requiring a high accuracy measurement, the user might need to provide a means of preserving a sample for later measurements at a laboratory.

For most tests carried out on-site, the water sample is tested without any sample pre-treatment other than, for example, 0.45 µm filtration

for toxic metals. This is then a filtered metal rather than a total analyte determination. However, some test-kits indicate sample pre-treatment procedures to obtain a "total analyte measurement". Often it is not practically possible to implement these procedures for in situ on-site measurements. The pre-treatment procedures are normally carried out in a designated room/area testing facility.

Documented sampling and sub-sampling procedures are essential to ensure that the test operative takes a fit-for-purpose relevant samples and sub-samples. These can be included in the actual test method. It is paramount that an appropriately-taken sample is used to then obtain a fit-for-purpose analysis.

It is important that the sample temperature at the time of testing is within the limits of the testing method. For example, the speed of reaction of many colorimetric reactions is significantly reduced at low temperatures.

Sampling from enclosed vessels and sample lines might be hazardous and documented safe working procedures should be available and undertaken correctly. This is particularly important where the system is operated at elevated temperatures and/or pressures.

Open-channel sampling (including sampling from boats) or other in-situ, on-site or remote site sampling requires specific documented safe working procedures that should be followed.

Samples should be taken at or below points of turbulence to provide representative samples.

In this British Standard, information on spot-sampling procedures predominates. Where on-site time- or flow-weighted composite sampling is required, the collection bottle should be refrigerated during and after the sampling period until the analysis is carried out. The composite sampling period should be kept to a minimum to reduce potential sample deterioration. However, note that some regulatory tests mention 24-hour composite samples. Where sample deterioration is a problem and regulations permit, it might be better to take a number of shorter period samples and then average the results (e.g. instead of one 24-hour composite sample, it might be better to use six 4-hour composite samples), assuming each composite sample is analysed promptly.

Turbidity and colour could interfere with many of the test methods described in this British Standard, particularly the colorimetric test methods. It can be advantageous or necessary to clarify visibly-turbid samples either by quiescent settlement then sampling the supernatant liquor or by filtration through a membrane or glass filter of known pore size. Details of any pre-treatment used should be recorded; simple purpose-designed, easy-to-use, low-cost, disposable systems for filtration on-site (e.g. syringe filtration) are commercially available. Any determinand present in the removed particulate matter will not be included in the test result. This information should be recorded and reported. It is not common practice in on-site testing of waters to pre-treat samples to solubilize particulate matter or release inactivated (bound) determinand. Such pre-treatments are not identified in the test methods cited in many BS 6068 water quality methods which typically measure only the soluble and reactive (available) determinand. Any pre-treatment is a matter for local decision, but should be clearly recorded and reported. Pre-treatment should only be used where such treatment does not invalidate the use

of the test method. Pre-treatment for some parameters (e.g. metals) might require the use of a designated room/area testing facility; this should be determined by a risk or COSSH assessment.

NOTE 2 Further details on sampling and sample preservation are described in BS 6068-6.7, BS 3285, BS 6068-6 and BS EN ISO 5667-3.

2.5 Selection and application of test methods

2.5.1 General

The test methods outlined in Annex A for use for on-site testing purposes should be adequate for most purposes. Most of the test methods included are based upon laboratory reference test methods but are commonly modified or utilized in a form to make them usable under on-site conditions. The selected test methods fall into three categories; colorimetric methods, titrimetric methods and instrumental analysis methods.

Commercial companies supply significant quantities of portable compact test-kits for water quality testing using a variety of techniques. The provision of test-kits is a competitive international market and variants of the same basic test method are commonplace between the different manufacturers. The primary factors when considering the use of commercial test-kits are accuracy, range, possible interferences, ease of use and possibly cost. Because of the scale of the international commercial test-kit market, there is no independent review of available systems. Manufacturers supply extensive information which is confined to their own products. This typically covers test method principle, test range, application areas in respect of test matrix, data on interferences, some typical best-case performance data and also health and safety information in respect of the reagents used. Detailed analytical performance data is not always provided. Defining standard testing conditions is difficult as there are currently no recommended test protocols for manufacturers to evaluate kit systems. It is important to appreciate that much manufacturer's data is best-case data, often related to aqueous standards. Users should always assess any new proposed test-kit that they intend to use against all relevant sample matrices that are to be tested. Where no validation data is available or the data is not relevant to the matrices of interest, the user should then carry out their own evaluation.

Because of their convenience and other defined advantages, the use of validated (see **3.4**) commercial test-kits is recognized for test methods outlined in this British Standard. The observations in this section are intended as a brief review of some of the important factors concerning commercial test-kits which will assist any consideration of their use.

2.5.2 Colorimetric methods

2.5.2.1 General

Colorimetric is the most widely used chemical testing technique for water quality test-kits. The format and principle of the kits available vary widely, as do the accuracy and discrimination achievable. Modern

microelectronics have assisted in the development of miniature portable colorimeters with a variety of facilities to aid simple use on-site, including direct concentration read-out. In contrast, the widely-used visual colour comparison systems remain cheap and simple, but are more operator-dependent in terms of accuracy and colour discrimination.

The following systems are widely available in different commercial formats:

a) visual comparison systems:
   1) paper test strips;
   2) printed colour comparator cards;
   3) colour comparison cubes;
   4) glass or plastics colour standard comparator discs; and
   5) sealed coloured liquid standards (ampoule/tube-based colour comparator);

b) portable photometers:
   1) digital read-out of transmission; and
   2) optical absorbance or concentration.

The concentration output is often derived from a calibration graph supplied by the test-kit manufacturer.

Commercial colour disc visual comparison systems, because of their simplicity and wide application are still used by many organizations as the basic system for many of the colorimetric test methods described in this standard. Alternative visual colour comparison formats are commercially available for most of the determinands measured by colorimetry and described within this British Standard, e.g. ampoule-based colour comparators, consisting of a number of vacuum sealed glass ampoules containing a harmless dye, each corresponding to the calibrated increment for the relevant test range. Ampoule/tube-based colour comparators typically come in two types, either a round comparator (containing e.g. 8 ampoules, in a small cylinder; the test ampoule is placed inside the cylinder and the whole apparatus held up to the light and viewed from the bottom, viewing the long path length along the axis of the ampoules) or a flat comparator (containing e.g. 9 ampoules, held in place against a flat, white plastic backing. The test ampoule is laid between the comparator ampoules to find the two closest colour matches, viewing the short path length across the axis of the ampoules).

Some test-kits incorporate reagents in a sample/measuring tube which can then be inserted directly into a comparator or photometer after adding the sample.

Low-cost, rugged, portable photometer-based methods are now widely available from manufacturers and provide an instrumental alternative to visual comparison for the majority of the colour tests outlined in this British Standard (see Annex B).

2.5.2.2 Operation and reagents

Many colorimetric test-kits have a shelf life up to three years, sometimes without refrigeration. Some test-kit manufacturers also offer “eco-friendly test-kits” which attempt to avoid the use of hazardous chemicals and minimize the overall carbon footprint.

However, users should always ensure that any method selected is fit for the intended purpose.

Many test-kits now contain all or virtually all the reagents necessary for the analysis to be performed in the actual measuring cell. This is typically an optical grade glass tube 12 mm to 15 mm in diameter that is inserted directly into the test-kit manufacturer's photometer. Any reagents that need to be added for the test are typically added via dose metered bottles, single volume automatic pipettes with disposable tips or rapidly dissolving tablets. This can help minimize operator error. Other systems use vacuum-sealed glass ampoules that contain the pre-measured chemistry reagent, and which do not require measuring or mixing of the reagent or measuring of the sample volume. Such ampoule-based systems draw the correct sample volume automatically into the ampoule, and further help to reduce operator error and increase the likelihood of repeatable results. The vacuum-sealed ampoule helps to keep the reagent fresh and ready for use and leads to test-kits with long shelf lives.

Many test-kits have a barcode on each of these measuring cells, the photometer then automatically selects the correct method of analysis. Again, this can help reduce potential operator error.

2.5.3 Visual comparator versus photometric detection

In this British Standard, colorimetric methods refer to methods that rely upon the absorption of light. This can be detected visually using colour comparators or electronically using a photometer. The cost of reliable fit-for-purpose photometers is now not that much greater than colour comparators. It is generally agreed that photometric measurements are more reliable and robust than the subjective visual comparison measurements as they reduce operator error, especially that due to colour discrimination.

It is important to emphasize that with visual colour comparison methods, precision and accuracy are dependent upon the visual acuity of the test-kit user and are also influenced by the environmental test conditions (e.g. ambient light intensity). Therefore meaningful comparative performance data (data trends or comparisons) might be less accurate than instrumental methods – more reliable, accurate and consistent results might be obtained using the equivalent on-site photometric method. The key criterion for selecting a technique is that all data generated should be fit-for-purpose.

While photometric analysis does offer an "anticipated" advantage over the visual colorimetric finish, this will not always be the case. There are some cases where detection for a particular method can be improved by the use of a longer path length than typically offered on handheld or even bench top photometers and spectrophotometers; the visual approach then offers an advantage as it greatly increases the practical cell path length. While a standard photometer can read up to approximately 20 mm cell path length using standard cell holders, colour comparators that use equivalent vacuum sealed glass ampoule comparators (containing a dye equivalent to a specific colour concentration standard), allow the analyst to "read" the colour on path lengths of 100 mm and 250 mm, depending on the comparator being used. Assuming good visual discrimination by the operator, this additional sensitivity might not be achievable with a commercially-available photometer or spectrophotometer. In the

analysis of trace levels of chemicals in water, where detection limits are critical, this added benefit could be advantageous.

Most visual test-kits for a given format are usable over a concentration range of about one order of magnitude, whilst a photometric method might be usable over a range of up to two orders of magnitude. The user will need to confirm the actual calibration range.

Most test-kit manufacturers supply both visual and photometric options for a given parameter. On-site photometric equipment is relatively inexpensive, reliable and robust. Results can be made fully traceable using the memory storage facilities of most photometers and might help avoid transcription errors. In addition, some commercial diode-array test-kit photometers permit simultaneous measurement at several different wavelengths. As turbidity is generally independent of the wavelength over the wavelength range of a typical absorption band, any turbidity present in the sample solution can be recognized by the photometer and automatically corrected.

2.5.4 Titrimetric methods

The titrimetric test methods described in this British Standard are normally based upon laboratory reference test methods which are identified within the described test methods described in Section **4**. To assist ease of use in on-site situations, only indicator colour end-point methods are described and instrumental end-points are not included. The test apparatus identified in the reference methods in Section **4** might not be suitable for use outside of a designated room/area testing facility.

Test-kit manufacturers now commonly supply alternative, more robust apparatus specifically designed for in situ on-site use. Commercial drop count or tablet count titrimetric test-kit methods are widely available.

Titrimetry is less widely used than colorimetry and typically it is less convenient to use and much less sensitive. There are a number of techniques used, depending on the accuracy and discrimination required, designed to increase the speed and convenience of in situ on-site titrimetry:

a) *Tablet count procedure*. This uses solid reagents, bound into a tablet together with indicator, as is the titrant and is based on the number of tablets added required to reach the end point in a known test portion of test sample.

b) *Drop count procedure*. This relies on counting the number of drops of titrant added from a special dropper used to reach the end point in a known test portion of test sample.

c) *Digital titrators*, with the titrant supplied in disposable plastics containers to fit the titrator. These give titration accuracy equivalent to the use of standard burettes but can be used in situ, on site. There are a number of titrators available which are hand-held and can be operated one-handed. Associated meters are available which can be programmed to give a direct readout of concentration.

d) *Reverse titration*. The indicator solution and reagent is contained inside a vacuum-sealed, self-filling ampoule. A flexible valve assembly is attached to the tip of the ampoule. The tip of the ampoule is snapped with the valve assembly in place. The tip

of the valve assembly is then immersed in the sample (using an optional titrettor), and small amounts of sample are drawn into the ampoule (the ampoule being gently rocked between each addition to ensure the reagent, indicator and sample are properly mixed) until the end point is reached. The ampoule is then inverted and the analyte concentration reading is read from the printed scale on the side of the ampoule.

2.5.5 Instrumental methods

NOTE An instrumental method is defined in this standard as a method that employs non-photometric instrumentation that can be used for in situ on-site measurements. It can also be used in a designated room/area testing facility analysis.

The instrumental test methods described in this British Standard are based upon laboratory reference test methods (the relevant BS is identified in the 'General' subclause of each method). Commercial instruments are not identified and only the general principles of the test instruments are described together with the test procedure. For all instrumental test methods described, instruments specially developed or adapted from laboratory systems are available for on-site use. Many parameters measured by instrumental test methods are temperature dependent. Wherever appropriate, on-site instruments should possess automatic temperature compensation and/or temperature measurement especially for "in-situ measurements".

Direct reading instruments for tests such as pH, turbidity, dissolved oxygen and electrical conductivity have portable equivalents to the fixed laboratory instruments specifically intended for testing external to the laboratory. Commercially available meters vary enormously in cost and degree of complexity. Most are battery operated, easily portable meters which are simple to use and with a read-out in direct concentration units. Fluoride analysis using an ion selective electrode (ISE) is only considered suitable for use in a designated room/area testing facility. (Haarhoff 2003 [16] and Noh and Coetzee 2006 [17])

2.5.6 Applicability of test methods

The test methods outlined in this British Standard have been chosen on the basis of being widely used to fulfil the circumstances and needs for on-site testing. Brief reference might also be made to alternative test methods or method formats within individual test methods which (depending on local circumstances) could be more applicable.

NOTE Some important determinands cannot be readily determined on-site because of method complexity and/or health and safety reasons. However, many of these can be determined in a designated room/area testing facility. Annex I identifies some of the tests that fall into this category.

2.5.7 Advantages and disadvantages of commercial test-kits versus laboratory testing

Assuming the available commercial test-kits for chemical testing of water quality are of acceptable performance as agreed with the user of the information, the advantages include:

a) no preparation of reagents is required;

b) greater safety results from pre-packaging of reagents;

c) convenience, speed and ease of use are improved with simplified techniques;

d) minimal sample deterioration from the use of fresh samples;

e) no need to develop in-house portable systems;

f) transport of kit and reagents is simpler and safer using the manufacturer's safety packaging;

g) frequency of testing and/or immediacy of test results for control purposes might be increased; and

h) the kit and reagents are readily stored and ready for use.

The disadvantages are chiefly involved with cost and the reliability and accuracy of the system, and include:

1) cost per test might be higher when using the more advanced commercial test systems; typically, commercial colour comparator or photometric test unit costs are relatively low when compared with small batches of laboratory tests;

2) the within batch and between batch reliability of test-kits for relevant matrices is sometimes not available from manufacturers; accuracy and reliability of the test-kits are probably inferior to reference test methods undertaken within a laboratory; however, they should be able to provide results of adequate accuracy and meet the principle of "fit-for-the-purpose-required"; it is the responsibility of the user to ensure that this is the case;

3) interferences might be incompletely documented and biased results might then be observed for some sample matrices; some test-kits do, however, document the most common intereferences.

2.5.8 Performance characteristics

Performance data for the test methods in this British Standard might be compromised by the conditions encountered external to the laboratory environment. Direct comparison of commercial test-kits and reference test methods using known standards and typical test samples provides useful test data to establish the precision and accuracy of the test method and the merit of using an alternative test-kit. It is prudent to perform control determinations to act as a supervisory confirmatory test for both the operator and test method. This will also verify the continuing performance of commercial test-kits. Periodic comparative testing should be undertaken using the test-kit and an experienced person using both standards and real samples. If discrepancies are observed efforts should be made to identify the causes of the discrepancy (e.g. the test-kit operator or the test-kit method).

The basic performance characteristics of the test-kit are usually supplied by the kit manufacturer.

2.6 Apparatus and equipment

2.6.1 General

Portability and safety are essential requirements for all test-kits used for on-site measurements. Apparatus and equipment fabricated from suitable plastics material are widely used and available as alternatives to conventional laboratory glassware.

Commonly, commercial kits are housed in custom-made carrying cases designed to improve the safety, portability and ease of use of test-kits. The test equipment provided with commercial test-kits is dependent on the test format selected. Test equipment associated with the various formats available is described in **2.6.2** to **2.6.5**.

2.6.2 Visual colour comparison test-kits

2.6.2.1 General

Test-kits are commercially available based on liquid, glass, plastics and printed card colour standards.

Competing systems differ in the number of colour standards provided, which affects the degree of discrimination afforded between individual concentration values. All the colour standards except for the printed standards are transparent standards. The accuracy achieved is very dependent on the ability of the manufacturer to achieve consistency, accuracy and long-term stability of representation of the colour and colour density of the standards. It also depends upon the discriminatory power in observing the colour by the test-kit user. Many test-kits employing visual measurements have low-cost portable photometer options which are not sensitive to ambient light levels or the visual acuity of the operator. It is generally accepted that these give more reliable results than equivalent visual methods.

2.6.2.2 Colour disc comparator system

The test equipment consists of a comparator unit which holds the colour disc and the test cuvettes for both blank and test samples. Both discs and cuvettes are interchangeable and are selected as specified by the test-kit manufacturer. The colour disc consists of a series of 8 to 10 discrete transparent glass or plastics standards, covering the test range, set around the circumference of the disc in ascending colour density. Alternatively, the entire disc is made of transparent glass or plastic which has a continuously increasing colour density gradient around its circumference. Both types are permanently marked in concentration units of the determinand being measured, equivalent to the colour density of the test solution. Background illumination aids for use where natural light levels are poor are available from most manufacturers of colour disc systems.

2.6.2.3 Liquid colour standards comparator system

The test equipment consists of a series of individual liquid colour standards, covering the test range, sealed into identical glass ampoules. Evacuated test ampoules containing the test reagents act as the test cuvettes and are identical to the standard ampoules. Up to 10 colour standards are provided ensuring colour discrimination equivalent to the colour disc system.

2.6.2.4 Colour cube comparator system

The test equipment is simple and consists of combined twin cuvettes. One cuvette is made up of a series of colour segments of ascending colour density. The sample is placed into the second empty cuvette and the appropriate reagents added, to allow direct visual

comparison. Where only a small number of colour segments are available, this limits the range and discrimination of the test method.

2.6.2.5 Printed colour card comparator system

The test equipment is usually minimal and consists of a card on which is printed a series of colour standards equivalent to the colours of the range of the test method. The colour standards are viewed through the blank solution until a colour match is achieved against the coloured-up test sample viewed against a white background. Colour matching by reflectance is typically not as exact as by transparency matching and additionally the colour printing needs to be exact. Colour standards might not be permanent – verification against known standards should be carried out on a regular basis.

NOTE Accurate results are very dependent on the ability of the manufacturer to represent correctly the colour and colour density of the colour standards and the person undertaking the test to discriminate differences between the colour of the standard and the colour of the test solution following addition of reagents. Also the colour (spectral distribution) of the incident light can also affect the accuracy of colour discrimination (due to the different response of the printed ink and the test solution).

2.6.3 Portable colorimeter systems

Test-kits incorporating portable colorimeters are very common. They provide consistent colour discrimination and eliminate the operator-dependence of comparator systems. Advances in microelectronics have allowed a significant amount of complexity to be incorporated within small hand-held instruments. Also, many systems allow storage of results that can subsequently be printed out or electronically downloaded. This helps to minimize transcription errors. Available systems vary significantly in cost and complexity but typically basic systems are not that much more expensive than the colour comparator test-kits. Selection is dependent on local requirements and needs.

Many test-kits now contain all or virtually all the reagents necessary for the analysis in the actual measuring cell. This is typically an optical grade glass tube 12 mm to 15 mm in diameter that is inserted directly into the test-kit manufacturer's photometer. Any reagents that need to be added for the test are typically added via dose-metered bottles, single-volume automatic pipettes with disposable tips or rapidly dissolving tablets. This should minimize operator error.

Many test-kits have a barcode on each of these cells, the photometer then automatically selects the correct method of analysis; this should reduce potential operator error.

Most test-kit photometers use narrow band interference filters with a photodiode detector or the more expensive versions can use a simple grating monochromator normally with photodiode or photodiode array (simultaneous multiwavelength detection).

2.6.4 Equipment for titrimetric on-site tests

Both complete test-kits and individual on-site-use burettes of innovative design are commercially available. The systems are designed for portability and ease of use and can be utilized for most standard

titrimetric tests. One simple option consists of a reverse titration test-kit employing a self-filling ampoule with valve assembly. Other titration test-kits options are available using a tablet count or drop count procedure, or a plastic burette with an integral titrant reservoir. Manual or electrically operated piston-based titrators with digital readout offer a greater degree of accuracy and ease of use. All manual or electrically operated piston based titrators should be regularly calibrated to ensure acceptable accuracy is maintained.

2.6.5 Equipment for instrumental tests

Advances in microelectronics have allowed the development of portable-use test equipment based on standard laboratory test equipment. There is a wide choice of commercially-available equipment. For example, turbidity; pH; dissolved oxygen, electrical conductivity; redox potential; anodic stripping voltammetry and fluorimetry. In the absence of formal testing protocols, selection of the most suitable equipment remains a local decision.

2.7 Reagents

2.7.1 General

Commercial ready-to-use test-kits/ready-made appropriate test-kit reagents should always be used for the test methods cited in this British Standard as this avoids preparing test reagents under non-laboratory conditions.

Distilled or RO/de-ionized water conforming to grade 3 of BS EN ISO 3696:1995 should be used.

If any reagents are prepared, chemicals of recognized analytical quality should always be used.

2.7.2 Pre-packaged reagents for colorimetric test-kits

These are supplied by the manufacturer and are specific to each manufacturer's own test-kit methods. Dependent on the manufacturer, these can be in liquid, powder or tablet form or a combination of different forms for different test methods. Pre-packaged reagents can also consist of single or mixed reagents. The reagents are not usually interchangeable between different systems and replacement refills for pre-packaged reagents should normally be obtained from the relevant test-kit manufacturer. Refills save the expense of purchasing an entire kit by permitting the reuse of major kit components.

Some of these products can have a long shelf life (e.g. up to three years, sometimes without refrigeration).

Some test-kit manufacturers also offer "eco-friendly test-kits" an attempt to avoid the use of hazardous chemicals and minimize the overall carbon footprint. However, users should always ensure that any method selected is fit for the intended purpose.

2.7.3 Pre-packaged reagents for titrimetric test-kits

The concentration of test-kit titration solutions are frequently different from the concentrations described in the reference

titrimetric test methods. They are usually more concentrated, to reduce the titrant volume used, because of the small capacity of reagent cartridges or reagent containers used in portable titrimetric test-kits. It is important to identify the correct calculation factors for the reagent strength used. A calculation factor is not, however, applicable for a reverse-titration test-kit as a scale is provided on the side of the ampoule, providing concentration reading in the units specified for that particular analyte.

Tablet, drop test and reverse-titration methods are alternative commercially-available simplified titrations. These test methods have lower analytical accuracy expectations than conventional laboratory titration techniques. These tests are dependent on the accuracy and reproducibility of the tablets or test drops, which depend on manufacturing tolerances. The titration skills of the test-kit user also affects the accuracy. Endpoint overshoot by adding too many tablets or test drops is another potential source of error. This is affected by the number of drop or tablet incremental additions. The greater the number of additions (i.e. the smaller the discrimination of each tablet or drop), the smaller the potential error.

2.7.4 Calibration and working standards

Water quality test-kits are intended for testing waters which usually lie in the pH range 4 to 10 and standard solutions should be within the same range, otherwise erroneous results might occur. Acid-based metal and metalloid standards might be unsuitable and alternative standards prepared from neutral salts should be used. Advice should be obtained from the relevant test-kit manufacturer where any doubt exists regarding suitable standards. Most test-kit manufacturers will supply suitable standard solutions. These should be used within their shelf-life.

2.7.5 Further background information on reagents

Both liquid and solid reagents used in test-kits are pre-packaged in a variety of formats and formulations. Solid reagents are supplied in powder form as individual powder pillows for individual tests and as bottles of powder containing a micro measuring spoon. Alternatively, solid reagents can be supplied in tablet form. In either form, the solid reagents can combine test reagents, indicators and interference suppressants. Liquid reagents are also supplied with some test-kits, either in dropping bottles or as reagent bottles from which aliquots are taken. A significant development in test-kit systems has been the packaging of measured doses of reagents, both liquid and solid, into individual capped tubes which act as disposable cuvettes designed for a single individual test. This has enhanced the ease and convenience of use, requiring in many cases only the addition of a specified aliquot of test sample. A novel modification of this system seals the reagents in evacuated glass vials which act as the cuvette. When the seal at the tip of the glass vial is broken beneath the surface of the sample, it automatically draws in a fixed volume of the sample rather than requiring a measured addition of sample by the analyst. Sealing under vacuum additionally prolongs the reagent shelf life.

Typically these single pre-packaged cuvettes for colorimetric determinations are made by manufacturers for use only with the portable colorimeters or comparators sold by that manufacturer.

However, portable colorimeters are now commercially available which can be self-programmed to use the majority of pre-packaged single test cuvettes available from different manufacturers.

Section 3: Quality assurance and quality control (QA/QC)

3.1 Introduction

Not all necessary QA/QC requirements might be covered by the instructions of the manufacturer of the test-kit. More QA/QC requirements might also be needed, even if the test-kit manufacturer complies with BS EN ISO 9001 and/or MCERTS.

3.2 Causes of "unfit-for-purpose" results

3.2.1 General

The main causes of unfit-for-purpose test-kit results are considered to be:

a) Incompetence of the operator (need for competence training).

b) Matrix interferences (although the initial method validation should indicate if this is a potential problem, it is not always possible to cover all potential extreme sample matrices that might be encountered).

c) Inappropriate method/test-kit employed (need a validated test-kit method that meets the client performance targets).

d) Contamination (need for principles of good laboratory practice to be understood and employed). This also includes carryover (**1.3.27**) caused by contamination of a subsequent sample by a previous sample, typically due to incomplete cleaning of a reused test-kit component.

e) Inappropriate sample pre-treatment (this needs to be agreed with the client).

3.2.2 Fitness-for-purpose-demonstration

In order to demonstrate fitness-for-purpose of the test-kit results, a hierarchical approach is recommended.

NOTE For example, the general approach outlined by the RSC Analytical Methods Technical Brief No. 28 (AMC 2007) [18].

a) *Calibration*. Test-kit instrumentation should be calibrated or verified at specified intervals (or prior to use) against measurement standards traceable to international or national standards; where no such standards exist, the basis for calibration or verification should be recorded.

b) *Qualification*. Qualification is the collection of documented evidence that an instrument performs suitably for its intended purpose and that it is properly maintained and calibrated. Use of qualified test-kit instruments in analysis contributes to confidence in the veracity of generated test-kit data.

c) *Validation* (See also **3.4**). Validation relates to the "fitness-for-purpose" of test-kit methods and associated analysis procedures. Ideally, this should include comparison data supplied by the test manufacturer that the test-kit method gives "equivalent" results to a fully characterized appropriate routine laboratory analysis

method for the parameter in question of a known and satisfactory performance for a range of relevant sample matrices. Any samples where there are significant discrepancies in the results should be checked using samples spiked with a known amount of the parameter by both methods to determine if one or both methods are in error.

A convenient illustration of this hierarchical approach is:

1) QC checks;
2) System suitability checks (**1.3.12**);
3) Analytical method validation;
4) Analytical instrument qualification [**3.2.2**b)].

3.2.3 Data integrity

A suitable framework for analytical data integrity is:

a) The test-kit instrumentation used has been qualified and calibrated.

b) The test-kit method selected is based upon sound scientific principles and has been shown to be robust, reliable and fit-for-purpose for the type of test materials being analysed under the conditions of use.

c) The test sample is representative and sufficiently close to homogeneous.

d) A person who is both competent and appropriately trained has carried out the analysis.

e) The integrity of the calculation used to arrive at the result and its uncertainty is correct and statistically sound.

f) Some form of internal quality control is carried out in every run of analysis. (A "run" is the period in which repeatability conditions prevail. This is typically a single batch of analysis where the user works without a break or without switching off any instrumentation. A quality control sample should be run at least every 20 samples.)

g) Some form of proficiency testing is undertaken whenever practicable.

h) Independent audits and assessments of the whole analytical system are carried out at intervals.

3.2.4 QA of on-site or test-kit methods

Similar to the routine analysis procedures employed in a laboratory, dependent upon the handling and nature of the method in question, the quality assurance of on-site or test-kit methods can be subject to very different requirements. In the case of a method which is used regularly (e.g. more than once per week), the same quality assurance measures can be similar to the reference method.

These include the following, and see DD ENV ISO 13530 and BS ISO 17381:

a) multiple testing;

b) measurements of standards and possible reference materials;

c) internal AQC (**1.3.21**), analysis of known samples or standards carried out with each batch of analysis and all the results are used to statistically control the procedure using Shewhart or equivalent charts;

d) plausibility tests by means of dilution and standard addition;

e) comparative tests with reference methods;

f) interlaboratory tests (proficiency testing);

g) keeping a control chart.

In the case of methods giving discrete analytical results, Shewhart or Range type control charts (see DD ENV ISO 13530 and Annex H) can be employed, whereas a target value chart is suitable for methods stating result ranges. In the first case, the control values are subject to statistical evaluation. In the latter, the control values are not subjected to statistical evaluation (mean value, standard error, control limits, warning limits) but instead it is decided whether or not they lie within a pre-defined tolerance range (yes/no decision). In this way, target value charts for blank values, mean values, recovery rates and range can be maintained.

In the case of occasional use (e.g. in the event of a fault in a waste-water facility), the points mentioned above would necessitate an excessive, not goal-oriented, degree of time and expenditure. However, personnel should, as far as possible, be fully trained in the use of the method and the test method should be characterized and validated in terms of its performance characteristics before it is used for the first time and periodic (e.g. monthly) checks made of performance throughout the life of the kit, and especially after maintenance of any test equipment. In certain individual cases, multiple testing, the measurement of standards and plausibility checks through dilution of real samples or standard addition are useful as simple check measures. Sample dilution and standard addition are particularly useful when sample matrix effects are either unknown or it is suspected that they might significantly influence the result of the test.

Finally, the selection of suitable quality assurance measures depends upon the specific aim of the analysis. The decision concerning the extent of the measures to be implemented, the results of these measures and their assessment should be documented.

All test-kit methods should be fully documented by the test-kit users and include how to take a representative and relevant sample, QA/QC procedures, relevant simple system suitability checks (SSCs) and should also include the author, version number of the documentation and the method approval date. SSCs are simple tests to ensure that the associated test-kit instrumentation is functioning within specified limits before commencing analysis. Each step in the method should be described sequentially and in full, should be unambiguous and written as simply as possible.

Relevant QA/QC protocols need to be drawn up by the test-kit user for their particular application. The manufacturer's instruction leaflet supplied with the test-kit might not be sufficiently detailed for carrying out fit-for-purpose analysis. Users should not rely on basic test-kit instructions alone, they might need to be rewritten to cover the context of the particular application and need to include sampling, sample preservation if required and sub-sampling and sample pre-treatment; all QA/QC aspects; as well as health and safety considerations with

respect to the test-kit, and disposing of any waste after carrying out the test. The test method supplied with the kit should form the basis of the method. All method documentation should be fully traceable and signed off by a responsible experienced person.

Consideration should be given to laminating/encapsulating documented methods used in the "outside environment," so they can more readily withstand adverse environmental conditions. Also this will assist in preventing unapproved amendments being subsequently added.

It is the responsibility of the organisation/person carrying out the test method to ensure that it is capable of producing results meeting the performance requirements of the client. The use of the test methods described in this British Standard should not be taken as a guarantee that results will be of sufficient accuracy or indeed even fit-for-purpose. Additionally, the performance of the test method used can be affected by both non-standard test conditions, principally variable environmental site conditions (e.g. high or low temperatures and/or extreme ambient light intensity) and most importantly by the capability and experience of the person using the test method. As a consequence, no performance data are given for individual test methods in this standard. Most test-kit manufacturers will provide "best case" performance data upon request. The performance data generated with the equivalent laboratory methods, for example in the series BS 2690 and/or BS 6068, can be used as a guide for method performance or method selection.

The vast majority of users of this standard will not be trained analysts and are likely to use commercial test-kits rather than prepare their own test-kits or devise on-site methods.

It is not possible to be totally prescriptive with respect to the amount of QA/QC to be employed for all on-site methods. On a pragmatic basis, the amount of QA/QC that can reasonably be carried out in situ on-site is generally somewhat less than can be carried out in a designated room/area testing facility or laboratory. Some simple screening methods that are detecting presence or absence of a given parameter or demonstrating that the concentration of a given parameter is significantly below a maximum permitted concentration will require less QA/QC than a method trying to assess the actual concentration of a regulatory parameter.

EXAMPLE: Below maximum permitted concentration.
Assessment of the chloride concentration of a sample prior to carrying out a COD test to ensure that the chloride level is below a stated concentration (chloride is a significant interferent in the test and test-kits are designed to cope with differing levels of interference).

EXAMPLE: Actual concentration.
Measurement of the actual COD of the sample.

Measurements of a single well-characterized industrial effluent will normally require less QA/QC than measurements on a wide range of much less characterized effluent samples from a number of different sources. Some useful information on screening methods is available (SWIFT 2003 [6]).

The organisation responsible for the analysis should justify the adequacy of the QA/QC protocols adopted in demonstrating the fitness for purpose of results for a particular analysis.

Pritchard and Barwick (2007) [19] have produced a very concise overview of quality assurance in analytical chemistry; users are

strongly recommended to consult this open learning textbook that should be of considerable benefit to non-analysts in understanding this key subject area.

3.3 Confidence interval considerations

EXAMPLE
Direct electronic-readout test-kit instrumentation might indicate a result for a given parameter of, for example, 51.2 mg/L sulfate, the user of the result might erroneously assume that the result is exactly 51.2 mg/L rather than 51.1 mg/L or 51.3 mg/L that has then been "rounded" to 51.2 mg/L. The result uncertainty, however, can often be as much as ± 20% of the concentration being measured for some test-kit parameters and can be higher. Assuming this to be the case in this instance, then this result would be better quoted as (51 ± 10) mg/L so the user can appreciate the uncertainty associated with the result.

Annex C gives an indication of the expected confidence intervals of top-of-the-range test-kits from two different manufacturers for the relevant manufacturer supplied quality control solutions. This Annex is only included in this standard for purely indicative purposes. Most major manufacturers of test-kits provide suitable QC standards with specified 95% confidence intervals for many parameters. These supplied QC test solutions can be directly traced back to national or international primary standards. If the user cannot meet their test-kit manufacturer's indicated confidence limits with the specified QC solutions, then a documented investigation should be carried out to determine the reasons for this and actions instituted to rectify the causes found.

Many commercial test-kits are also able to provide some indicative basic performance data. If this is not readily available, then the user should contact the manufacturer and if this information cannot be provided, then the user should seriously consider using an alternative test-kit where this information is available. This should be regarded as "best case" data as it is usually obtained from matrix-free standards. Performance in real sample matrices could be significantly worse.

3.4 Method validation (Assessing method performance characteristics)

3.4.1 Evaluation

A test-kit should be formally evaluated by the user in terms of:

a) Concentration range.

b) Accuracy/bias using typical sample matrices to be tested by appropriate spiking. A worst case matrix should be included.

NOTE Cheeseman et al. (1989) [20] give further advice on this issue.

c) Within and between batch precision for typical relevant water sample matrices.

d) Method detection limit.

e) Potential sample matrix interference effects.

f) Linearity of the calibration function.

g) Operator bias (this would include visual acuity tests if relevant).

h) Test-kit reproducibility (between different batches of test-kits). This information would normally be supplied by the test-kit manufacturer.

i) Speed of analysis.

j) If the test-kit is to be used on-site outside of a designated room/area testing facility, then the likely extreme temperatures and the variation in ambient light considerations need to be taken into account. (e.g. some colorimetric reactions proceed much slower at 4 °C than at the normal laboratory or designated room/area testing facility temperature of approximately 20 °C). Tests should be carried out on some standards at just below the lowest temperature likely to be encountered. Also the effect of bright sunlight should be assessed on colorimetric methods. and artificial light or low levels of natural light on visual comparison methods.

k) QA/QC targets and system suitability (SSCs) checks of the analysis.

l) Training and experience needed by test-kit users.

The results of this evaluation should then be formally documented.

3.4.2 Validation under typical operating conditions

If possible, a series of standards, a blank, a range of typical samples and some spiked samples should be run on-site under typical operating conditions with the test-kit. Then, all the tested samples should be brought back to a laboratory and tested again under laboratory environmental conditions, with minimal delay.

At the same time, the same set of samples should be analysed using an equivalent fully characterized appropriate routine laboratory analysis method procedure. This should demonstrate if the test-kit on-site results agree with test results obtained under defined laboratory environmental conditions. It will also show if the test-kit method gives equivalent results to a laboratory-equivalent routine, validated method. It should be appreciated that unstable determinands can result in an apparent positive bias of on-site measurement relative to the subsequent laboratory results. In this instance, it is the lab-based results that are biased rather than the on-site measurements.

If this is considered too onerous for the application, then a series of standards, a blank, a range of typical samples with the parameter of interest concentration at less than 30% of the calibration range and then the same samples spiked with 50 – 70% of the calibration range should be run.

Method performance targets should then be set up for all relevant measurements (confidence limits for blanks, standards and recoveries). Some test-kit manufacturers provide spiking solutions for their test-kits that can be used to detect measurement errors caused by the effect of the sample matrix on the sensitivity (i.e. sample matrix bias effects). These spiking solutions can also be prepared in a suitable designated room/area testing facility or a laboratory if they are not available from the test-kit manufacturer.

3.4.3 Critical concentration spiking and detection

Ideally, a typical sample with a low or negligible level of analyte should be spiked with the analyte using a spiking addition equivalent to the regulatory or critical concentration.

Other bias effects can be reduced by appropriately pre-treating the sample (e.g. filtering the sample to remove suspended solids for parameters such as chloride, sulfate, nitrite, ammonia or chloride) using photometric final detection. These parameters are unlikely to be associated with any suspended solids in the sample, so removal of the solids should not affect the result.

3.4.4 Blanks

A sample-specific blank value for a photometric method can be obtained by carrying out the cuvette test, replacing the colour reaction reagent with RO/DI water, on a sample and then measuring the sample. The result is attributable purely to the characteristics of the sample (turbidity/colour), and is subsequently deducted from the result of the analysis using the actual sample.

3.4.5 Adsorbed metals

Many toxic metals in natural waters and effluents tend to be adsorbed on to suspended particulate matter at neutral sample pH values and (in order to determine the total amount present in the sample) might require an acid digestion step followed by filtration and neutralization if a colorimetric method is to be employed. Careful consideration of the key aspect of sample pre-treatment is required before any method is adopted. For river and raw water metal analysis, the filtrate from a 0.45 µm filtered sample is usually analysed – this determines the dissolved (available) metals. The filtration should be carried out at the time of sampling.

3.5 Routine quality control

There is a need to ensure fit-for-purpose analysis on a long-term on-going basis: basic system suitability checks (SSCs) should be run for each batch of analysis; an appropriate blank and QC should also be run. Then, on a regular basis (e.g. weekly or monthly) check spike recovery on a typical sample (as described above). All data should be recorded on suitable control sheets or charts. Many test-kit manufacturers will supply suitable standards and spiking solutions.

The action limit values on the QC chart for test-kits will often be fixed limits agreed with the result end user rather than statistically derived from the method validation data. This is considered adequate for test-kit usage for many simple applications, but might not be sufficient when the value of the result is critical. Arbitrary warning limits can also be set up for simple applications if required.

For applications where the value of the result is critical (e.g. regulatory monitoring or trend monitoring), a full Shewhart-type control chart or charts should be used with statistically derived limits.

All QC failures should be fully investigated as to the reason for the failure and the investigation findings and any remedial action instituted should be recorded.

With very few exceptions (e.g. redox potential and pH), a result of "zero" should never be quoted. The appropriate validated less than (detection limit) value should always be cited. Where a result of zero is appropriate it should be stated as 0 or 0.0 or 0.00 etc. depending on the precision of the result.

All users should seriously consider participating in a relevant proficiency testing scheme: some test-kit manufacturers run such schemes for certain of their test-kits, third party testing comparison results are useful for confirming on-going fitness-of-purpose results. All failures should be fully investigated as to the reason for failure and the investigation, findings and any remedial action instituted should be recorded.

The primary purpose of routine quality control checks is to give early indication of a problem and instigate an investigation and corrective action. If carried out correctly and proper records of investigations and actions kept, it also provides demonstration of continuing fitness for purpose of results.

3.6 Target test-kit requirements

Before selecting a test-kit for a given parameter, users should carefully consider with the users of the data, the target requirements (including sampling considerations and performance characteristics) that are needed to obtain fit-for-purpose results in all sample matrices likely to be encountered. These requirements should then be carefully documented and formally agreed with the final end user(s) of the data. Then the test-kit performance requirements should be discussed with the test-kit supplier with respect to the range of sample matrices likely to be encountered to help ensure that an appropriate fit-for-purpose test-kit is employed.

Annexes D and E set out examples of how this might be set out in a simple pro-forma, both for a parameter analysed in a designated room/area testing facility and for a parameter analysed on-site at the actual sampling location. These pro formas then need to be assessed and signed off when considered satisfactory. Obtaining the data to complete the pro forma can be carried out either by the user or (if they have the necessary facilities) then some of the data can be obtained by a competent laboratory, after discussions with the test-kit user. If the targets set cannot be met with the chosen test-kit, then either a more appropriate test-kit should be selected and tried or the target specification might be relaxed with the agreement of the end user. The competent laboratory might also be able to cite performance data generated using the equivalent laboratory methods, for example those in the series BS 2690 or/and BS 6068, can be used as a guide for method performance. The test-kit user will also have to demonstrate competence in using the test-kit as part of their training (see Annex A).

The most important factor is that both the user of the test-kit and the primary user of the results from the test-kit are aware of the basic performance characteristics of the test-kit and any limitations.

Major manufacturers of test-kits provide advice on QA/QC and as stated previously many also provide suitable QC standards with specified confidence intervals. In addition, some provide spiking solutions for their test-kits that can be used to detect measurement errors caused by the effect of the sample matrix (i.e. bias effects) (see **1.3.7**). Some manufacturers supply secondary standards for checking the wavelength accuracy and linearity of the absorbance of the photometer as well as simple portable electronic temperature sensor for temperature control and calibration of heating blocks.

Also photometric standards are available for checking the calibration of pipettes on-site by pipetting the supplied standard into a specified volume volumetric flask and diluting to volume with water and measuring the absorbance at a specified wavelength on the test-kit photometer.

The routine QA/QC that should be employed needs careful consideration and should never be overlooked and should always form part of the test-kit user's training.

Annexes F and G set out examples of how this might be set out in a simple pro forma for test room/area and general on-site parameters. Annex H gives an example of a control chart. Some parameters might require a modified form. These pro formas then need to be assessed and signed off when considered satisfactory. The data required to complete the pro forma should be obtained by the trained user of the test-kit with each batch of analysis and immediately documented.

3.7 Concentration ranges of methods

The application range of a test method should be stated by the test-kit manufacturer in their literature or test-kit instructions. The stated range in many cases can be extended by pre-dilution of the test sample or (where the result is independent of the sample volume) a smaller test portion can be used. Depending on local requirements, results can be quoted as "less than" for concentrations below a stated level, or "greater than" for concentrations above a stated level. These upper and lower "levels of interest" should be clearly defined wherever they are applied. Where more than one application range is necessary for any determinand, alternative test methods for the different ranges might be required. For visual colour comparator methods, the user often needs to estimate readings falling between two adjacent colour discs - this is not necessary when photometric measurements are made as a discrete figure is displayed.

3.8 Interferences

Because of the wide range of water types covered in this British Standard the information given on interferences is not comprehensive. There is always the possibility that the water under test might contain substances which will interfere with the test procedure. Test method parameter summaries listed in Annex H identify typical interfering substances, but (in order to keep test methods as simple and as easy to use as possible) information on procedures for overcoming interferences is not always included. The most common interference, particularly for colorimetric test methods, is turbidity, which can easily be identified. The removal of turbidity and the manner of its removal is dependent upon local conditions (see also **2.5.3**). Where the test method is similar or traceable to an existing ISO/CEN/British Standard, reference might be made to the standards for information on overcoming interferences. Pre-packaged reagents might include reagents designed to minimize or eliminate known interferences. Commercial test-kit systems might also indicate sample pre-treatment requirements designed to overcome interferences. Realistically, most of these need to carried out in a designated room/area testing facility (see **2.3**).

Section 4: Titrimetric methods for use in a designated room/area testing facility

*COMMENTARY ON SECTION **4***
*It is important to emphasize that in titrimetric methods the precision and accuracy are considerably influenced by the environmental test conditions. However, with the use of a designated test room/area equivalent results to that of a conventional laboratory might be obtained with appropriately trained personnel. The use of titrimetric commercial test-kits suitable for on-site testing are covered in Section **4**.*

*The test procedure and apparatus required for reverse titration based test-kits where the sample is titrated against a fixed volume of appropriate reagent(s) are not described in Section **4**. This is because these test-kits require no pre-measurement of a sample aliquot and follow a simplified test methodology. Small volumes of sample are taken up using a simple ball-valve assembly on the tip of an evacuated ampoule containing the appropriate reagents until the colour changes, indicating the equivalence point of the titration Quantitative results are obtained by reading the scale off of the graduated ampoule. [See also **2.5.4** d)].*

*Reverse titration test-kits are described in **2.5.4, 2.6.4** and **2.7.3**. Reverse titration test-kits are currently available for all the analyte tests specified in Section **4**, with the exception of **4.6** Sulfate and **4.8** Zinc.*

4.1 Determination of alkalinity

4.1.1 General

This method is based on BS 2690-109. The quantitative capacity of aqueous media to react with hydrogen ions is known as alkalinity.

The alkalinity of a water is primarily a function of the bicarbonate, carbonate, and hydroxide concentrations. This method measures the alkalinity due to the presence of each of the three anions.

Commercial titrimetric test-kits based on the same principle are available. They typically employ novel titration systems in place of conventional burettes and also use modified test reagents (see **2.7.3**).

4.1.2 Scope of this method

This test method is recommended as a designated room/area testing facility test for the determination of alkalinity. It is applicable to potable, raw and lightly polluted waters.

The analytical range for alkalinity is from 2.0 mg/L to 500 mg/L expressed as calcium carbonate ($CaCO_3$) using a test portion of 100 mL. The range might be extended using smaller test portions. Where the total volume of titrant exceeds 50 mL the test is repeated using a smaller test portion.

NOTE Strongly coloured or turbid solutions interfere with the colorimetric end-point.

Chemically treated waters can include other ions such as phosphate, silicate and borate which affect the pH of the sample and the measurement of alkalinity.

Oxidizing agents present in the sample might bleach indicators.

4.1.3 Principle

Titration of test sample with standard acid to the visually determined end-point values of 8.3 pH units and 4.5 pH units. These end-points are the selected equivalence points for the alkalinity determinations of the three principal anions. Titration with acid against phenolphthalein to pH 8.3 represents titration of all hydroxide and conversion of carbonate to bicarbonate and is defined as the alkalinity to phenolphthalein (*P*). Titration with acid against methyl orange from pH 8.3 to pH 4.5 represents the titration of the bicarbonate to carbonic acid. An alternative to methyl orange is bromocresol green/methyl red indicator. The combined total titration with acid down to pH 4.5 is defined as the total alkalinity (*T*).

In chemically treated waters containing added ions, for example phosphate, silicate and borate, the alkalinity to phenolphthalein titration (*P*) can be affected by the added ions. Barium chloride ($BaCl_2$) is added to suppress the effect of the added ions and both the alkalinity to phenolphthalein titration (*P*) and the modified alkalinity to phenolphthalein titration (P_B) need to be measured. The latter is a measure of the caustic alkalinity only and, in conjunction with the measurement of alkalinity to phenolphthalein (*P*), allows the total alkalinity to be calculated. The alkalinity due to the presence of different anions can also be calculated (see Table 1).

*NOTE 1 The total alkalinity end-point (T) is fixed at pH 4.5. The pH at which equivalence is reached is higher at low ionic strength and might not be at pH 4.5 for samples of low alkalinity (see **4.1.7**).*

NOTE 2 For the purposes of this method, alkalinity can be defined as the quantitative capacity of aqueous media to react with hydrogen ions.

4.1.4 Reagents

*NOTE The standard volumetric solution (**4.1.4.2**) and test indicator solutions used for this test are commercially available and are recommended for designated room/area testing facility testing (see **2.3**). A modified calculation formula is necessary where alternative titrant concentrations apply (see **2.7.3**). Please also note that the reverse titration method does not use the concentrations of reagent specified in this subclause on account of its different test methodology. In addition, the reverse titration test-kits for Total (T) Alkalinity may use bromocresol green/methyl red indicator in place of methyl orange indicator.*

4.1.4.1 *Distilled or de-ionized water*. (See **2.7.1**.)

4.1.4.2 *Sulfuric acid standard volumetric solution*, c (H_2SO_4) = 0.01 mol/L, standardized by titration against a standard sodium carbonate solution, well stoppered and is stable for at least one month.

4.1.4.3 *Phenolphthalein indicator*, 1.0 g of phenolphthalein, dissolved in 100 mL of ethanol, diluted to 200 mL with water and mixed.

4.1.4.4 *Mixed indicator*, 0.200 g of bromocresol green and 0.015 g of methyl red, dissolved in 100 mL of ethanol and mixed. The indicator is stored in an amber bottle.

4.1.4.5 *Methyl orange indicator*, 0.05 g of methyl orange dissolved in 100 mL of water.

4.1.4.6 *Barium chloride*, 10% (*v/v*), 11.7 g of barium chloride ($BaCl_2.2H_2O$) dissolved in water and diluted to 100 mL. The solution is stable indefinitely.

4.1.4.7 *Sodium sulfate crystals*, ($Na_2SO_4.10H_2O$).

4.1.5 Apparatus

4.1.5.1 *Titration flask*, of about 250 mL capacity (for some reverse titration methods, a sample cup filled to the 20 mL mark is sufficient).

4.1.5.2 *Burette*, of 50 mL capacity, or a suitable alternative on-site titration system (see **2.6.4**).

4.1.6 Samples and sampling

Samples should be analysed with the minimum of delay after sampling and should not be stored for subsequent testing (see **2.4**). Samples should be collected in a polyethylene or borosilicate glass bottle which should be filled to overflowing with minimal turbulence and stoppered to exclude air.

4.1.7 Procedure

Measure a suitably sized test portion of sample (V_0), in millilitres, not exceeding 100 mL, into the titration flask (**4.1.5.1**) and, as necessary, dilute to 100 mL with water. Add about four drops of phenolphthalein indicator (**4.1.4.3**) and titrate the solution with sulfuric acid (**4.1.4.2**) until the disappearance of any pink colour. Note the titrant volume (V_1) in millilitres. Where no pink colour is obtained record the volume as zero.

NOTE 1 This is the phenolphthalein end-point (P).

Add about four drops of the mixed indicator (**4.1.4.4**) to the solution from the first titration and continue the titration with sulfuric acid (**4.1.4.2**) until a change from green-blue to a light pink occurs. Record the total titrant volume (V_2) in millilitres.

NOTE 2 This is the total alkalinity end-point (T).

As an alternative to the second titration step, methyl orange indicator (**4.1.4.5**) can be used instead of the mixed indicator (**4.1.4.4**) for low alkalinity samples.

*NOTE 3 Methyl orange indicator gives a more correct definition of the total alkalinity equivalence point than the mixed indicator at low alkalinities but its end-point is less sharp and more difficult to see and the mixed indicator (**4.1.4.4**) is recommended for more strongly buffered samples.*

For measurement of alkalinity to phenolphthalein after the addition of barium chloride, (P_B), measure a fresh test portion of the sample (V_0), in millilitres, into a clean titration flask and, as necessary, dilute to 100 mL with water. Add about four drops of phenolphthalein indicator (**4.1.4.3**) followed by a crystal of sodium sulfate (**4.1.4.7**) and 1.0 mL of barium chloride (**4.1.4.6**). Swirl the flask gently for 2 min and then titrate the solution with sulfuric acid (**4.1.4.2**) until the disappearance of any pink colour. Note the titration volume (V_3) in millilitres. Where no pink colour is obtained record the volume as zero.

4.1.8 Expression of results

4.1.8.1 Alkalinity to pH 8.3

The phenolphthalein alkalinity (*P*) (expressed as milligrams per litre of $CaCO_3$) should be calculated using the equation:

$$P = \frac{V_1 \times 1\,000}{V_0}$$

where

V_1 is the titrant volume of sulfuric acid solution, $c(H_2SO_4)$ = 0.01 mol/L, to pH 8.3 (in mL);

V_0 is the test portion of sample (in mL).

4.1.8.2 Alkalinity to pH 4.5

The total alkalinity (*T*) (expressed as milligrams per litre of $CaCO_3$) should be calculated using the equation:

$$T = \frac{V_2 \times 1\,000}{V_0}$$

where

V_2 is the total titrant volume of sulfuric acid solution, $c(H_2SO_4)$ = 0.01 mol/L, to pH 4.5 (in mL);

V_0 is the test portion of sample (in mL).

Table 1 **Alkalinity relationship**

			All values are in milligrams per litre of $CaCO_3$	
Titrations	**Hydroxide alkalinity**	**Carbonate alkalinity**	**Bicarbonate alkalinity**	**Total alkalinity**
$P = 0$	0	0	T	T
$2P < T$	0	$2P$	$T - 2P$	T
$2P = T$	0	$2P$	0	T
$2P > T$	$2P - T$	$2(T - P)$	0	T
$P = T$	T	0	0	T
$P > P_B$	P_B	$2(P - P_B)$	0	$2P - P_B$
$P_B = 0$	0	$2P$	(No correlation)	

Where

P is the phenolphthalein alkalinity;

T is the total alkalinity;

PB is the phenolphthalein alkalinity after addition of barium chloride.

These relationships are affected if significant quantities of phosphate or other interfering anions are present. Alkalinity values should be reported to the nearest whole number as milligrams per litre of $CaCO_3$.

4.1.8.3 Alkalinity to pH 8.3 in the presence of barium chloride

The modified alkalinity to phenolphthalein (P_B) (expressed as milligrams per litre of $CaCO_3$) should be calculated using the equation:

$$P_B = \frac{V_3 \times 1\,000}{V_0}$$

where

V_3 is the titrant volume of sulfuric acid solution, $c(H_2SO_4)$ = 0.01 mol/L, to pH 8.3, after addition of barium chloride (in mL);

V_0 is the test portion of sample (in mL).

NOTE Conversion factor: 1 mL of sulfuric acid solution, $c(H_2SO_4)$ = 0.01 mol/L, = 1.0 mg of alkalinity expressed as $CaCO_3$.

4.1.9 Performance characteristics

Meaningful comparative performance data are not readily obtainable under on-site conditions (see commentary at the start of Section **4**).

The suitability of commercial test-kit versions of this method incorporating pre-packaged test reagents can be established by comparative analysis of test samples and reference solutions under laboratory conditions using both the test-kit method and this recommended test method.

4.2 Determination of calcium and total hardness

4.2.1 General

The tests are based on BS 6068-2.8 for calcium hardness and BS 6068-2.9 for total hardness. Commercial titrimetric test-kits based on the same principles are available for both calcium and total hardness. They typically employ novel titration systems in place of conventional burettes and also use modified test reagents (see **2.7.3**).

This test method measures calcium separately and calcium plus magnesium concentrations of a water.

Typically the hardness of natural water is due to the calcium and magnesium salts present and it is convention to regard calcium hardness as a measure of the calcium content and to regard total hardness as a measure of the calcium plus magnesium content in a water. Both are expressed in terms of concentration of calcium carbonate.

4.2.2 Scope of this method

This test method is recommended as a designated room/area testing facility test for the determination of calcium and total hardness of waters. It is applicable to potable, raw and industrial waters.

The analytical range for hardness is from 5 mg/L to 400 mg/L expressed as calcium carbonate ($CaCO_3$) using a test portion of 50 mL. The range can be extended by using a smaller test portion. Where the total volume of titrant exceeds 20 mL, it is necessary to repeat the test using a smaller test portion as necessary (see **4.2.7**).

NOTE A number of metal ions if present in excess will interfere either because they titrate as calcium and magnesium or because they obscure the end-point colour change. Similarly, very dark samples might obscure the end-point colour change. Where necessary, samples have to be returned to a laboratory for analysis.

4.2.3 Principle

*COMMENTARY ON **4.2.3***
For the purposes of this method, hardness is defined as a property of water manifested by resistance to the development of a lather with soap. It is due mainly to the presence of calcium and magnesium ions.

4.2.3.1 Calcium hardness

Calcium ions are complexed by titration with ethylenediaminetetra-acetic acid (EDTA) disodium salt at a pH value above 12. Free calcium ions are completely complexed at the end-point, which is detected using a complexiometric indicator that gives a distinct colour change in the absence of free calcium. Magnesium is precipitated at pH values above 12 as the hydroxide and does not react with the EDTA titrant.

4.2.3.2 Total hardness

Calcium and magnesium ions are complexed by titration with ethylenediaminetetra-acetic acid (EDTA) disodium salt at a pH value of about 10. Free calcium and magnesium ions are completely complexed at the end-point causing a distinctive colour change in the complexiometric indicator in the absence of free calcium and magnesium. The magnesium content of the water can be calculated by difference.

4.2.4 Reagents

*NOTE The standard EDTA reagent (**4.2.4.4**), pH 10 buffer (**4.2.4.3**) and calcium and total hardness indicators (**4.2.4.5**, **4.2.4.6**) are commercially available. Commercial alternatives might be available for the buffer solution and hardness indicators. It is the responsibility of the analyst to ensure alternative reagents give acceptable results before use. A modified calculation formula is necessary where alternative titrant concentrations apply (see **2.7.3**).*

4.2.4.1 Distilled or deionized water (see 2.7.1)

4.2.4.2 *Sodium hydroxide solution*, *c*(NaOH), 2 mol/L. 8.0 g of sodium hydroxide (NaOH) should be dissolved in about 20 mL of water. The solution should be cooled, diluted to 100 mL with water in a one-mark volumetric flask, and stored in a polyethylene bottle.

4.2.4.3 *Buffer solution*, pH 10 ± 1, 67.5 g of ammonium chloride (NH_4Cl) should be dissolved in 570 mL of concentrated ammonia solution, density about 0.880 g/mL, with 5.0 g of EDTA, disodium magnesium salt ($C_{10}H_{12}N_2O_8Na_2M_g$), added and the solution diluted to 1 000 mL in a one-mark volumetric flask. Stored in a tightly stoppered polyethylene bottle, the reagent shelf life is about 2 months.

10 mL of buffer diluted to about 100 mL with water gives a pH of 10 ± 0.1.

4.2.4.4 *EDTA volumetric solution*, *c*(Na_2EDTA) = 0.01 mol/L.3.722 g of EDTA, disodium salt ($C_{10}H_{142}O_8Na_2.2H_2O$), dried for 1 h at 80 °C, dissolved in water and diluted to 1 000 mL in a one-mark volumetric flask. The solution, stored in a polyethylene bottle, is stable for at least 2 months.

4.2.4.5 *Calcium hardness indicator*, Patton and Reeders indicator powder. 0.2 g of 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid, mixed thoroughly by grinding with 100 g of sodium chloride (NaCl).

NOTE This reagent is commercially available in tablet form.

4.2.4.6 *Total hardness indicator*, Eriochrome Black indicator solution. 0.5 g of the sodium salt of Eriochrome Black T (1-(1-hydroxy-(2-naphthylazo)-6-nitro-2-naphthyl-4-sulfonic acid), dissolved in 100 mL of triethanolamine $(HOCH_2CH_2)_3N$. Up to 25 mL of ethanol can be added to reduce solution viscosity. The solution is stored in a glass bottle and discarded when the end-point colour change deteriorates.

4.2.5 Apparatus

4.2.5.1 *Titration flask*, of about 250 mL capacity.

4.2.5.2 *Burette*, of 25 mL capacity, or an equivalent alternative on-site titration system (see **2.6.4**).

4.2.6 Samples and sampling

Samples should be analysed with the minimum of delay after sampling and should not be stored for subsequent testing (but see note to **4.2.2**).

4.2.7 Procedure for calcium hardness

Measure a test portion of 50 mL or a smaller volume (V_0), in millilitres, of the test sample diluted to 50 mL into the titration flask (**4.2.5.1**). Add 2 mL of sodium hydroxide (**4.2.4.2**) and about 0.2 g of calcium hardness indicator (**4.2.4.5**) (or its commercial equivalent).

Mix the solution and titrate immediately with EDTA titrant (**4.2.4.4**) to the visible end-point colour change.

NOTE A blue colour with a red tinge is observed on approaching the end-point which is reached when the red tinge disappears and a pure blue colour remains.

Note the titrant volume (V_1), in millilitres.

4.2.8 Procedure for total hardness

Measure a test portion of 50 mL or a smaller volume (V_2), in millilitres, diluted to 50 mL into the titration flask (**4.2.5.1**). Add 4.0 mL of buffer solution (**4.2.4.3**) and three drops of total hardness indicator (**4.2.4.6**) (or its commercial equivalent).

Mix the solution and titrate immediately with EDTA titrant (**4.2.4.4**) to the visible end-point colour change.

NOTE A change from red to blue is observed near the end-point which is reached when the last red tinge disappears and a pure blue colour remains.

Record the titrant volume (*V*3), in millilitres.

4.2.9 Expression of results

The calcium hardness *CH* (expressed as milligrams per litre $NCaCO_3$) should be calculated using the equation:

$$CH = \frac{V_1 \times 1\,000}{V_0}$$

where

V_1 is the titrant volume of EDTA solution, $c(Na_2EDTA)$ = 0.01 mol/L (in mL);

V_0 is the test portion of sample (in mL).

The total hardness *TH* (expressed as milligrams per litre of $CaCO_3$) should be calculated using the equation:

$$TH = \frac{V_3 \times 1\,000}{V_2}$$

where

V_3 is the titrant volume of EDTA solution, $c(Na_2EDTA)$ = 0.01 mol/L (in mL);

V_2 is the test portion of sample (in mL).

NOTE Conversion factor:1 mL of EDTA solution, $c(Na^2EDTA)$ = 0.01 mol/L = 1.0 mg of calcium or calcium plus magnesium expressed as $CaCO_3$.

Magnesium hardness = total hardness minus calcium hardness (expressed as milligrams per litre of $CaCO_3$).

4.2.10 Performance characteristics

Meaningful comparative performance data are not readily obtainable under on-site conditions (see commentary at the start of Section **4**). The suitability of commercial test-kit versions of this test method incorporating pre-packaged test reagents might be established by the comparative analysis of test samples and calcium carbonate standards under laboratory conditions using both the test-kit method and this recommended method.

4.3 Determination of chloride

4.3.1 General

This method is based on BS 6068-2.37. Commercial titrimetric test-kits based on the same principle are available. They typically employ novel titration systems in place of conventional burettes and also use modified test reagents (see **2.7.3**).

4.3.2 Scope of this method

This test method is recommended as a designated room/area testing facility test for the determination of chloride. It is applicable to potable, raw, industrial and lightly polluted waters.

The analytical range for chloride is from5 mg/L to150 mg/L, using a test portion of 100 mL. The range can be extended using a smaller

test portion. Where the total volume of titrant exceeds 25 mL it is necessary to repeat the test using a smaller test portion.

NOTE Strongly coloured or turbid solutions interfere with the colorimetric end-point. Substances which form insoluble silver compounds including bromide, iodide, cyanide and sulfide or which complex with silver ions give enhanced chloride values. Reducing agents such as sulfite and hydrazine might affect the functioning of the indicator. This effect is overcome by the addition of a few crystals of ammonium persulfate prior to the addition of the indicator.

4.3.3 Principle

Titration of the test sample at pH 5 to pH 9.5 with standard silver nitrate. The silver ions react with the chloride ions present to precipitate quantitatively insoluble silver chloride. Addition of a small excess of silver nitrate forms a red brown silver chromate between the free silver ions and chromate ions added as an indicator, which defines the end-point.

NOTE One reverse titration test-kit uses mercuric nitrate with a diphenylcarbazone indicator.

4.3.4 Reagents

*NOTE The standard reagent solution and test indicator solution used for this test are commercially available and are recommended for designated room/area testing facility testing (see **2.3**). A modified calculation formula is necessary when alternative titrant concentrations apply (see **2.7.3**).*

4.3.4.1 *Distilled or deionised water*. (See **2.7.1**).

4.3.4.2 *Silver nitrate standard volumetric solution*, $c(AgNO_3)$ = 0.02 mol/L. 3.397 g of silver nitrate ($AgNO_3$), previously dried at 105 °C, dissolved in water and diluted to 1 000 mL in a one-mark volumetric flask. The solution is light-sensitive and has to be stored in a brown glass bottle with a glass stopper. The solution is stable for at least 3 months.

4.3.4.3 *Potassium chromate indicator solution*, 10 g ± 1 g of potassium chromate (K_2CrO_4) dissolved in water and diluted to about 100 mL.

4.3.4.4 *Ammonium persulfate*, $(NH_4)_2S_2O_8$, solid.

4.3.5 Apparatus

4.3.5.1 *Titration flask*, of about 250 mL capacity.

4.3.5.2 *Burette*, of 25 mL capacity or a suitable alternative on-site titration system (see **2.6.4**).

4.3.6 Samples and sampling

Samples should be analysed with the minimum of delay after sampling and should not be stored for subsequent testing (see **2.4**).

4.3.7 Procedure

Measure a test portion of 100 mL, or a smaller volume (V_0), in millilitres, of the test sample diluted to about 100 mL with water, into the titration flask (**4.3.5.1**).

If the pH of the sample or diluted sample is not in the range 5.0 to 9.5 as determined using pH indicator papers or a pH meter adjust the pH value with dilute nitric acid or sodium hydroxide as necessary.

Add about four drops of potassium chromate indicator (**4.3.4.3**). Titrate the solution with silver nitrate (**4.3.4.2**) until the first appearance of a permanent reddish-brown colour. Record the titrant volume (V_1) in millilitres.

4.3.8 Expression of results

The chloride content *CC* (expressed in milligrams per litre of chloride) should be calculated using the equation:

$$CC = \frac{V_1 \times 709}{V_0}$$

where

V_1 is the titrant volume of silver nitrate solution, $c(AgNO_3)$ = 0.02 mol/L (in mL);

V_0 is the test portion of sample (in mL).

NOTE Conversion factor:1.0 mL of silver nitrate solution, $c(AgNO_3)$ = 0.02 mol/L, = 0.709 mg of chloride.

4.3.9 Performance characteristics

Meaningful comparative performance data are not readily obtainable under on-site conditions (see commentary on Section **4**). The suitability of commercial test-kit versions of this test method incorporating pre-packaged test reagents can be established by comparative analysis of test samples and reference solutions under laboratory conditions using both the test-kit method and this recommended test method.

4.4 Determination of free carbon dioxide

4.4.1 General

The direct titrimetric method described in this British Standard uses titration of free carbon dioxide (CO_2) with sodium carbonate. The reference laboratory test procedure is BS 2690-109, which involves gas stripping and absorption with standard sodium hydroxide of the free CO_2. Commercial titrimetric test-kits using direct titrimetry are available. They typically employ novel titration systems in place of conventional burettes and also use modified test reagents (see **2.7.3**). The reverse titrimetric method uses titration of free carbon dioxide (CO_2) with sodium hydroxide.

4.4.2 Scope of this method

This test method is recommended as a designated room/area testing facility test for the determination of free carbon dioxide. It is applicable to potable, raw and industrial waters.

The analytical range for free carbon dioxide is from 0 mg/L to 200 mg/L, using a test portion of 100 mL. The range can be extended using a smaller test portion. Where the total volume of titrant exceeds 25 mL it is necessary to repeat the test using a smaller test portion.

NOTE Weak bases including amines and salts of weak acids and strong bases also react with sodium carbonate and give enhanced values. Samples with high concentrations of dissolved solids including saline waters give negatively biased values.

4.4.3 Principle

Free carbon dioxide reacts with added sodium carbonate to form bicarbonate. The conversion to bicarbonate is complete at pH 8.3 and the end-point is determined using phenolphthalein colour indicator.

4.4.4 Reagents

*NOTE The concentrated stock reagent solution and indicator solution used for this test are commercially available and are recommended for designated room/area testing facility testing (see **2.3**). A modified calculation formula is necessary where alternative titrant concentrations apply (see **2.7.3**).*

4.4.4.1 *Distilled or de-ionized water*, (see **2.7.1**) where necessary, the water is rendered free of CO_2 by boiling and cooling prior to use.

4.4.4.2 *Sodium carbonate stock standard solution*, $c(Na_2CO_3)$ = 0.1 mol/L. 5.30 g of sodium carbonate (Na_2CO_3), previously dried at 105 °C, dissolved in about 100 mL of freshly boiled and cooled water and diluted to 500 mL in a one-mark volumetric flask using freshly boiled and cooled water. This solution is retained in a tightly stoppered container.

4.4.4.3 *Sodium carbonate standard volumetric reagent solution*, $c(Na_2CO_3)$ = 0.02 mol/L. Prepared by dilution of stock solution (**4.4.4.2**) volumetrically with water that is free of carbon dioxide and freshly prepared by boiling and cooling before use. The solution is stored in a tightly capped bottle to prevent absorption of carbon dioxide and prepared as required.

4.4.4.4 *Phenolphthalein indicator solution*, 1.0 g of phenolphthalein, dissolved in 100 mL of ethanol and diluted to 200 mL with water.

4.4.5 Apparatus

4.4.5.1 *Titration flask*, of about 250 mL capacity.

4.4.5.2 *Burette*, of 25 mL capacity or a suitable alternative on-site titration system (see **2.6.4**).

4.4.6 Samples and sampling

Samples should be analysed with the minimum of delay after sampling and should not be stored for subsequent testing (see **2.4**).

Care should be taken to minimize absorption or loss of carbon dioxide on sampling and subsequent transfer and analysis of the test portion. Where possible the sample bottle should be flushed by displacement and filled to overflowing.

4.4.7 Procedure

Measure a test portion of 100 mL or a smaller volume (V_0), in millilitres, if necessary, into the titration flask (**4.4.5.1**).

Add about 10 drops of phenolphthalein indicator (**4.4.4.4**) and immediately titrate the solution with sodium carbonate solution (**4.4.4.3**), swirling or stirring gently, until a faint persistent pink colour which is the end-point appears. Note the titrant volume (V_1) in millilitres.

4.4.8 Expression of results

The carbon dioxide content *CD* (expressed in milligrams per litre of CO_2) should be calculated using the equation:

$$CD = \frac{V_1 \times 880}{V_0}$$

where

V_1 is the titrant volume of sodium carbonate standard volumetric solution, $c(Na_2CO_3)$ = 0.02 mol/L (in mL);

V_0 is the test portion of sample (in mL).

NOTE Conversion factor:1.0 mL of sodium carbonate standard volumetric solution, $c(Na_2CO_3)$ = 0.02 mol/L, = 0.88 mg of CO_2.

To convert milligrams per litre of CO_2 to milligrams per litre of $CaCO_3$, multiply the test result as free CO_2 by 2.27.

4.4.9 Performance characteristics

This designated room/area testing facility test is subject to potential error because of enhancement by other ions and loss or absorption of carbon dioxide. Meaningful comparative performance data are not readily obtainable under on-site conditions (see commentary to Section **4**).

The suitability of commercial test-kit versions of this test method incorporating pre-packaged test reagents and of this recommended on-site test method can be established by comparative analysis of test samples under laboratory conditions by either or both test methods and by BS 2690-109.

4.5 Determination of nitrite

4.5.1 General

Sodium nitrite and nitrite-based proprietary compounds are widely used as anticorrosion additives in industrial cooling systems. The nitrite content requires frequent checking because of chemical or microbiological degradation. This test method is a procedure for control testing based on a classical text book oxidation-reduction titrimetric reaction. One equivalent commercial test-kit system is currently available and commercial systems using alternative oxidation reagents are available for determination of nitrite-dosed waters.

4.5.2 Scope of this method

This test method is recommended as an on-site method for the determination of nitrite. It is applicable to nitrite-treated industrial waters.

The analytical range for nitrite is up to 1 500 mg/L expressed as sodium nitrite, using a test portion of 50 mL. Where the total volume of titrant exceeds 25 mL, it is necessary to repeat the test using a smaller test portion.

NOTE Other reducing agents, such as sulfite and ferrous ion, which are also oxidized by ceric sulfate gives enhanced nitrite values and are likely to interfere at the normal levels encountered.

4.5.3 Principle

The sample is acidified and titrated with standard ceric sulfate solution to oxidize the nitrite (NO_2^-) content present. The end-point of the titration is identified by added ferroin redox indicator which changes from orange to a pale pure blue colour.

NOTE Other oxidizing agents such as potassium permanganate and potassium dichromate can be used as the titrant, using appropriate indicators. Ceric sulfate has the advantage of being very stable in solution over prolonged periods. Other test methods are available, including visual and photometric test-kits using azo dye formation chemistry.

4.5.4 Reagents

*NOTE All the reagents used in this test method are commercially available ready-made and are recommended for designated room/area testing facility testing. (See **2.3**). A modified calculation formula is necessary where alternative titrant concentrations apply (see **2.7.3**).*

4.5.4.1 *Distilled or de-ionized water*. (See **2.7.1**).

4.5.4.2 *Sulfuric acid*, 10% (V/V). 50 mL of concentrated sulfuric acid, added cautiously, with stirring, to about 300 mL of water. The solution is cooled and diluted to 500 mL. The solution is stable indefinitely.

4.5.4.3 *Ceric sulfate standard volumetric solution*, $c(Ce(SO_4)_2)$ = 0.1 mol/L. 40.430 g of cerium (IV) sulfate ($Ce(SO_4)_2.4H_2O$) added to about 50 mL of water and about 25 mL of concentrated sulfuric acid added cautiously with stirring. The solution is gently warmed until the solid has all dissolved, and diluted to 1 000 mL in a one-mark volumetric flask. The solution is stable for at least 3 months.

4.5.4.4 1,10-*Phenanthroline ferrous complex (ferroin) indicator*. This reagent solution is commercially available and is stable indefinitely.

4.5.5 Apparatus

4.5.5.1 *Titration flask*, of about 500 mL capacity.

4.5.5.2 *Burette*, of 25 mL capacity, or a suitable alternative on-site titration system (see **2.6.4**).

4.5.6 Samples and sampling

Samples should be analysed with the minimum of delay after sampling and should not be stored for subsequent testing (see **2.4**).

4.5.7 Procedure

Measure a test portion of 50 mL, or a smaller volume (V_0), in millilitres, of the test sample diluted to about 50 mL, into the titration flask (**4.5.5.1**).

Add 10 mL of sulfuric acid (**4.5.4.2**) to the solution and swirl to mix. Add about five drops of ferroin indicator (**4.5.4.4**) and titrate the solution slowly, swirling gently, with ceric sulfate solution (**4.5.4.3**) to a pale blue colour which persists for at least 10 s at the end-point. Note the titrant volume (V_1) in millilitres.

4.5.8 Expression of results

The nitrite content *NC* (expressed in milligrams per litre of $NaNO_2$) should be calculated using the equation:

$$NC = \frac{V_1 \times 3\,500}{V_0}$$

where

V_1 is the titrant volume of ceric sulfate standard volumetric solution, $c(Ce(SO_4)_2)$ = 0.1 mol/L (in mL);

V_0 is the test portion of sample (in mL).

NOTE Conversion factor:1 mL of ceric sulfate = 3.5 mg of sodium nitrite ($NaNO_2$). To convert units of $NaNO_2$ to NO_2^-, use a multiplication factor of 0.67.

4.5.9 Performance characteristics

Meaningful comparative performance data are not readily obtainable under on-site conditions (see commentary to Section **4**). The presence of reducing agents other than nitrite will give positively biased results.

4.6 Determination of sulfate

4.6.1 General

The test is based on method B of SCA Bluebook *Sulfate in waters, effluents and solids:Methods for the examination of water and associated materials* [21], which includes the use of ion exchange to remove interfering cations.

For technical reasons, the use of ion exchange is omitted from this standard (see **4.6.9**).

4.6.2 Scope of this method

This test method is a designated room/area testing facility test for the determination of high sulfate levels. It is applicable to industrial boiler waters.

Using a test portion of 10 mL, the analytical range for sulfate extends from 140 mg/L to 1 400 mg/L of sulfate as SO_4. The range can be extended by using smaller test portions. Lower ranges can be measured using larger test portions, but interferences might then become unacceptable.

NOTE Strongly coloured and turbid solutions interfere with the colorimetric end-point.

Substances which form insoluble compounds or complexes with the added barium ions will give enhanced sulfate results. The principle interferences are orthophosphate and cations which complex with the EDTA titrant. Where high interference levels are known or suspected, the test samples have to be tested in a laboratory using an appropriate method.

4.6.3 Principle

Sulfate ions in the test sample are quantitatively precipitated by the addition of excess barium chloride solution. The residual excess barium is determined by titration, with ethylenediaminetetra-acetic acid (EDTA) disodium salt using a complexiometric colour indicator, at high pH. The barium combined as barium sulfate is calculated and is an indirect measure of the sulfate content of the sample. There is also a photometric self-filling ampoule based test-kit for the determination of sulfate ions in aqueous solutions available, employing a barium chloride reagent in an acidic solution.

4.6.4 Reagents

4.6.4.1 *Distilled or de-ionized water*, (see **2.7.1**).

4.6.4.2 *Barium chloride solution*, *c*($BaCl_2$) = 0.01 mol/L. 2.443 g of barium chloride ($BaCl_2.2H_2O$) dissolved in about 500 mL of water. 2.0 mL of concentrated hydrochloric acid is added and the solution diluted to 1 000 mL in a one-mark flask with water. The solution is stable for at least 6 months.

4.6.4.3 *EDTA volumetric solution*, *c*(Na_2EDTA) = 0.01 mol/L. 3.722 g of ethylenediaminetetra-acetic acid disodium salt dried for 1 h at 80 °C, dissolved in water and diluted to 1 000 mL in a one-mark flask with water. The solution is stable for at least 2 months.

NOTE This solution is commercially available.

4.6.4.4 *Buffer solution*, 200 mL of ethanolamine (C_2H_7ON), reagent grade, added to 800 mL of industrial methylated spirits. The reagent is stable for at least 3 months.

4.6.4.5 *Complexiometric indicator*. 0.15 g of orthocresolphthalein complexone (metalphthalein), 0.08 g of Naphthol Green B and 20 g of potassium chloride (KCl), ground together to form a uniform fine-grained mixture. The solid reagent is stable for at least 1 year.

4.6.5 Apparatus

4.6.5.1 *Titration flask*, of about 250 mL capacity.

4.6.5.2 *Burette*, of 25 mL capacity, or a suitable alternative on-site titration system (see **2.6.4**).

4.6.6 Samples and sampling

Samples should be analysed with the minimum of delay after sampling and should not be stored for subsequent testing (see **2.4**). Sample bottles should be filled to overflowing to exclude air and eliminate air oxidation of any sulfite present.

4.6.7 Procedure

Measure a test portion of 10 mL, or a smaller test volume (*V*0) diluted to 10 mL, containing not more than 14 mg of sulfate, into the titration flask (**4.6.5.1**).

Add 15 mL of barium chloride (**4.6.4.2**) slowly to the titration flask, swirling to mix the solution during the addition. Then add 25 mL of the buffer solution (**4.6.4.4**) and swirl the solution to mix.

Add about 0.1 g of the complexiometric indicator (**4.6.4.5**) to give a strong purple colour to the solution.

Titrate the solution with EDTA volumetric solution (**4.6.4.3**) to the visible end-point colour change.

NOTE The colour fades rapidly near the end-point which is reached when there is a sharp change to pale green.

Record the titrant volume (V_1) in millilitres.

Repeat the complete test using water in place of the test sample and record the titrant volume (V_2) in millilitres. The volume of barium chloride added is the same in both the tests.

4.6.8 Expression of results

The sulfate content *SA* (expressed in milligrams per litre as SO_4^{2-}) should be calculated using the equation:

$$SA = \frac{V_2 - V_1 \times 961}{V_0}$$

where

V_0 is the test portion of sample (in mL);

V_1 is the sample titration of EDTA volumetric solution, $c(Na_2EDTA)$ = 0.01 mol/L (in mL);

V_2 is the blank titration of EDTA volumetric solution, $c(Na_2EDTA)$ = 0.01 mol/L (in mL).

NOTE Conversion factor:1 mL of EDTA volumetric solution, $c(Na_2EDTA)$ = 0.01 mol/L, = 0.961 mg of SO_4^{2-}.

4.6.9 Performance characteristics

Meaningful comparative performance data are not obtainable under on-site conditions (see Commentary to Section **4**).

The omission of the ion exchange stage makes this subject to some interference procedure. The non-removal of cations which interfere in the test might produce unacceptably biased results using this test method.

4.7 Determination of sulfite

4.7.1 General

The test is based on method 4500-SO3 B of *Standard methods for the examination of water and wastewater* [22]. Commercial titrimetric test-kits based on the same principle are available. They typically

employ novel titration systems in place of conventional burettes and also use modified test reagents (see **2.7.3**).

4.7.2 Scope of this method

This test method is recommended as a designated room/area testing facility test for the determination of sulfite. It is applicable to potable, raw, industrial and lightly polluted waters.

The analytical range for sulfite extends from 5 mg/L to 150 mg/L, using a test portion of 250 mL. The range can be extended using a smaller test portion. Where the total volume of titrant exceeds 50 mL it is necessary to repeat the test using a smaller test portion.

NOTE Other reducing agents such as iron (II) and sulfide react with iodine giving enhanced sulfite values.

4.7.3 Principle

The test sample is acidified and titrated with standard potassium iodide-iodate solution. The free iodine liberated by the iodide-iodate solution reacts with sulfite quantitatively. The reaction end-point is given when the first excess of iodine after the quantitative oxidation of the sulfite reacts with starch indicator to give a blue colour.

4.7.4 Reagents

*NOTE The standard volumetric solution and starch indicator solution used for this test are commercially available and are recommended for designated room/area testing facility testing (see **2.3**). A modified calculation formula is necessary where alternative titrant concentrations apply (see **2.7.3**).*

4.7.4.1 *Distilled or de-ionized water*, (see **2.7.1**).

4.7.4.2 *Sulfuric acid*, 50% (V/V).

4.7.4.3 *Potassium iodide-iodate standard volumetric solution*, $c(KI/KIO_3)$ = 0.02 mol/L. 0.713 g of potassium iodate (KIO_3), previously dried for 2 h at 105 °C, 7.0 g of potassium iodide (KI) and 0.5 g of sodium hydrogen carbonate ($NaHCO_3$), dissolved in water. The solution is diluted to 1 000 mL in a one-mark volumetric flask. The solution is stable for at least 3 months.

4.7.4.4 *Starch indicator solution*, 1 g of soluble starch should be mixed into a smooth paste with cold water and added, with stirring, to about 200 mL of boiling water. The mix is cooled and decanted into a glass bottle. The indicator is discarded when organisms growing on the starch become visible.

NOTE Proprietary commercial iodine indicators are a recommended alternative.

4.7.5 Apparatus

4.7.5.1 *Titration flask*, of about 500 mL capacity.

4.7.5.2 *Burette*, of 50 mL capacity, or a suitable alternative on-site titration system (see **2.6.4**).

4.7.6 Samples and sampling

Samples should be analysed with the minimum of delay after sampling and should not be stored for subsequent testing (see **2.4**). To minimize atmospheric oxidation the sample bottle should be flushed, preferably by displacement, and filled by overflowing. Hot samples should be stoppered and allowed to cool to below 30 °C.

4.7.7 Procedure

Measure a test portion of 250 mL, or a smaller volume (V_0), diluted to about 250 mL with water into the titration flask (**4.7.5.1**).

Add 2.0 mL of sulfuric acid (**4.7.4.2**) (see note to **4.7.4**) and 1.0 mL of starch indicator (**4.7.4.4**) to the flask and swirl the solution briefly. Immediately titrate the solution with potassium iodide-iodate solution (**4.7.4.3**) to an initial permanent faint blue colour, ignoring subsequent colour discharge. Record the titrant volume (V_1) in millilitres.

*NOTE For highly alkaline test samples (see **4.1**), the alkalinity has to be neutralized with sulfuric acid (**4.7.4.2**) then a further 2.0 mL added prior to the addition of starch indicator (**4.7.4.4**) and subsequent titration.*

4.7.8 Expression of results

The sulfite concentration *SU* (expressed in milligrams per litre of SO_3^{2-}) should be calculated using the equation:

$$SU = \frac{V_1 \times 800}{V_0}$$

where

V_1 is the potassium iodide-iodate standard volumetric solution, $c(KI/KIO_3)$ = 0.02 mol/L, (in mL);

V_0 is the test portion of sample (in mL).

NOTE Conversion factor:1.0 mL of potassium iodide-iodate standard volumetric solution, $c(KI/KIO_3)$ = 0.02 mol/L = 0.80 mg of SO_3.

To convert the units from SO_3^{2-} to Na2, SO_3^{2-}, use a multiplication factor of 1.58.

4.7.9 Performance characteristics

Meaningful comparative performance data are not readily obtainable under on-site conditions (see commentary to Section **4**).

The suitability of commercial test-kit versions of this test method incorporating pre-packaged test reagents can be established by comparative analysis of test samples and reference solutions under laboratory conditions using both the test-kit method and this recommended method.

4.8 Determination of zinc

4.8.1 General

This method is based on a published method (Hickey and Overbeck [23]), for which there is no known equivalent reference method.

Existing alternative methods for zinc lack either acceptable specificity or simplicity for adoption for on-site use.

4.8.2 Scope of this method

This test method is recommended as an on-site control method for the determination of zinc. It is applicable to raw and industrial waters and measures both soluble and colloidal zinc.

The analytical range for zinc extends from 0.5 mg/L to 20 mg/L using a test portion of 100 mL. Where the total volume of titrant exceeds 20 mL it is necessary to repeat the test using a smaller test portion.

NOTE Iron and copper both react with the chelating agent. Copper is masked by the prior addition of sodium thiosulfate but concentrations in excess of 1 mg/L cause excessive interference with the colour indicator.

4.8.3 Principle

The test sample is titrated with diethylenetriaminepenta-acetic acid (DTPA), which selectively chelates zinc in the presence of calcium in a solution buffered to pH 4.5. The reaction end-point is given when dithizone indicator changes to blue-green indicating that all the zinc is complexed. Photometric test-kits using a self-filling ampoule are also available for the determination of zinc in aqueous solutions, using zincon reagent in a buffered alkaline solution to form a blue complex.

4.8.4 Reagents

4.8.4.1 *Distilled or deionised water*, (see **2.7.1**).

4.8.4.2 *Buffer solution*, pH 4.5. 270 g of sodium acetate ($CH_3COONa.3H_2O$) dissolved in water and 225 mL of glacial acetic acid (CH_3COOH) added. The solution is diluted to 1 000 mL in a one-mark volumetric flask. The solution is stable indefinitely.

4.8.4.3 *Dithizone indicator solution*, 0.4 % (m/m). 0.4 g of dithizone indicator dissolved in 100 mL of methanol, prepared fresh every week.

4.8.4.4 *Diethylenetriaminepenta-acetic acid standard volumetric solution*. 0.6017 g of diethylenetriaminepenta-acetic acid (DTPA) dissolved in water and 8.5 mL of sodium hydroxide solution, c(NaOH) = 1.0 mol/L, added. The solution is diluted to 1 000 mL in a one-mark volumetric flask.

4.8.4.5 *Sodium thiosulfate solution*, 5% (*m/m*). 5.0 g of sodium thiosulfate ($Na_2S_2O_3.5H_2O$) dissolved in water and diluted to 100 mL in a one-mark volumetric flask. The reagent is sufficiently stable at least for one month for use as a masking agent.

4.8.4.6 *Propan-2-ol (isopropyl alcohol) general-purpose grade reagent*.

4.8.5 Apparatus

4.8.5.1 *Titration flask*, of about 500 mL capacity.

4.8.5.2 *Burette*, of 25 mL capacity, or a suitable alternative on-site titration system (see **2.6.4**).

4.8.6 Samples and sampling

Samples should be analysed with the minimum of delay after sampling and should not be stored for subsequent testing (see **2.4**).

4.8.7 Procedure

Measure a test portion of 100 mL, or a smaller volume (V_0) of the test sample diluted to 100 mL into the titration flask (**4.8.5.1**).

Add 5.0 mL of buffer solution (**4.8.4.2**) and 0.5 mL of sodium thiosulfate solution (**4.8.4.5**) and swirl the solution to mix. Add 100 mL of propan-2-ol (**4.8.4.6**). Add 0.5 mL increments of the dithizone indicator solution (**4.8.4.3**) until the solution colour remains strongly pink and then titrate the solution with DTPA solution (**4.8.4.4**) until the solution changes from pink to blue-green at the end-point. Record the volume of titrant (V_1) in millilitres.

NOTE The dissolved zinc content only may be determined by pre-filtration of the sample through a membrane filter of pore size 0.45 µm to remove colloidal zinc. The result may then be reported as soluble (filtered) zinc.

4.8.8 Expression of results

The zinc concentration Z (expressed in milligrams per litre) should be calculated using the equation:

$$Z = \frac{V_1 \times 100}{V_0}$$

where

V_1 is the titrant volume of standard volumetric solution, DTPA (in mL);

V_0 is the test portion of sample (in mL).

NOTE Conversion factor:1.0 mL of DTPA standard volumetric solution = 0.1 mg of zinc.

4.8.9 Performance characteristics

See commentary to Section **4**; the precision and accuracy are considerably influenced by environmental test conditions. The suitability of this test method can only be established by comparison with results from appropriate test samples using conventional laboratory test methods for zinc determination.

Section 5: Instrumental methods

*COMMENTARY ON SECTION **5***
An instrumental method is defined in this standard as a method that employs non-photometric instrumentation that can be used for in situ on-site measurements. It can also be used in a designated room/area testing facility analysis.

5.1 Determination of dissolved oxygen

5.1.1 General

There are now two main commercial instrumental methods for dissolved oxygen, the well-established method based on BS EN 25814, an electrochemical probe method, and the newer luminescent dissolved oxygen (phosphorescence decay) (LDO) method. Depending on local requirements and on the type of instrument employed, measurement is made either as concentration or as percentage saturation of dissolved oxygen in the sample, or both. Both systems are suitable for rapid in-situ discrete measurement on site, but can also be used for continuous monitoring. Both instrumental procedures are not affected by high levels of particulate matter in the sample, which can seriously interfere with the titrimetric or colorimetric test methods.

As the majority of the method sections are effectively the same for both systems, to avoid repetition the two methods have been combined with separate sections describing each system.

5.1.2 Scope of this method

This test method is recommended as an on-site test for the determination of dissolved oxygen: it is applicable to all types of waters including saline waters. Depending on the instrument, measurement of dissolved oxygen can be made either as concentration of dissolved oxygen, as milligrams per litre or micrograms per litre of oxygen, or as percentage saturation of dissolved oxygen, or both. The method measures oxygen in water corresponding to 0% to 100% saturation and commonly instruments permit readings up to 200% saturation to allow for oxygen supersaturation. The solubility of oxygen in water is dependent on the temperature and salinity of the sample and the atmospheric pressure. The required corrections in many instances are relatively small and for routine measurement purposes are ignored, depending on local requirements. Alternatively, instruments are commercially available which can automatically compensate for temperature and/or pressure and/or salinity. Instruments are commonly multi-range to allow for both high and low dissolved oxygen concentrations.

NOTE Interferences consist of matter in the sample including solvents, oils and algae which attack or obstruct the membrane or phosphorescent probe surface. Also, gases other than oxygen, including gaseous halogens and hydrogen sulfide, might diffuse through the membrane.

5.1.3 Principle

5.1.3.1 Electrochemical probe method.

A measuring probe, consisting of a small galvanic or polarographic electrochemical cell enclosed by a selective gas permeable membrane, is immersed in the water to be analysed. Oxygen passing through the membrane is reduced at the anode and the current produced is directly proportional to the partial pressure of oxygen in the sample at a given temperature. Modern instruments usually include automatic temperature compensation. Dissolved oxygen (DO) concentrations in milligrams per litre of oxygen measured at pressures other than normal atmospheric pressure are not affected by the pressure difference. However, the solubility of oxygen is dependent on atmospheric pressure and the dissolved oxygen displayed as percentage solubility by a meter will require the observed reading to be compensated to allow for pressure differences. Modern meters might incorporate pressure transducers in their circuitry which automatically compensate for pressures other than normal atmospheric pressure (USGS 2006 [24]).

Electrochemical measurement methods determine the current or voltage resulting from the reduction of oxygen to hydroxide ions at the cathode. To compensate for this "oxygen consumption", oxygen molecules diffuse continuously in the electrolytes. Depletion of the oxygen molecules in the direct vicinity of the sensor can only be prevented by keeping the sample in motion around the sensor. The method is relatively simple to use and is well-suited to making discrete or continuous in situ measurements of DO concentration in surface or groundwaters. The method performance can be negatively affected by calibration drift; by loose, wrinkled, or damaged membranes; or by sensor contact with hydrogen sulfide. Unfortunately, poor performance can occur without any indications from the instrument readings (USGS 2006 [24]), so the following checks should be made before each use.

Before each time it is used on-site, the following checks should be made.

a) The instrument batteries and all electrical connections should be checked.

b) The sensor should be inspected closely, checked for a loose, wrinkled, or torn membrane, air bubbles beneath the membrane, and for a tarnished or discoloured cathode or anode. If any of these problems are detected, the sensor should not be used until it has been serviced according to the manufacturer's recommendations.

c) Test instrument calibration. An instrument that fails to calibrate properly should not be used. The instrument should be serviced according to the manufacturer's recommendations and recalibrated.

d) The instrument should be tested to ensure that it will read zero in a freshly prepared zero DO solution. If the instrument reading exceeds 0.2 mg/L, then the sensor membrane and electrolyte (if present) need to be replaced or the sensor needs to be repaired. Before repairing or replacing the sensor, the zero DO reading should be rechecked again with a freshly prepared zero DO solution.

e) Recalibration should follow the manufacturer's recommendations.

5.1.3.2 Luminescent dissolved oxygen (LDO) – Sensor technology method

The luminescent sensor employs a light-emitting diode (LED) to provide a brief incident light pulse, which excites an oxygen-sensitive luminescent-dye molecule substrate (luminophore) of the sensor. After dissipation of the excitation energy, longer-wavelength light is emitted (luminescence). The average luminescent lifetime is measured by the sensor and is inversely proportional to the DO concentration in the water. A time measurement is used to determine the dissolved concentration. There are two methods for doing this:

a) the pulsed lifetime method, which utilizes an excitation source with a pulse termination time that is shorter than the lifetime of the emission lifetime(s) being evaluated; and

b) the phase-shift method, which employs a sinusoidally modulated excitation source combined with phase-sensitive detection. The modulated emission is delayed in phase by an angle φ, relative to the excitation beam. The phase shifts are easy to measure, since the phase shift varies monotonically with oxygen concentration.

Neither method requires prior knowledge of the complexity of the decay(s) measured. Thus suspended matter and highly coloured samples have minimal effect upon the response. There are no consumables such as membranes or filling solutions with the LDO method, unlike the electrochemical methods.

The technology does not consume oxygen at the sensor-water interface; therefore, no stirring is required in slow or stagnant water. The LDO method involves no oxygen consumption. The oxygen molecules simple have to stay in contact with the oxygen-sensitive layer. The sample does not have to be kept in motion around the sensor.

There are no known sources of interference to the method in natural aquatic systems.

Luminescent-based sensors are pre-calibrated by the manufacturer and most manufacturers' literature suggests that no further calibration is warranted. The accuracy of factory calibrations, however, might not satisfy the data-quality objectives of a specific programme. Frequency of calibration can have a significant effect on the overall accuracy and precision of DO measurements; therefore, users of these meters are advised to make frequent calibration checks and to recalibrate as frequently as required to meet specific data-quality objectives.

NOTE There is a potential issue here caused by the change to the percentage saturation (% sat) readings with atmospheric pressure. If the definition of 100% sat is fixed to the partial pressure of oxygen at a known pressure, e.g. 760 mm Hg (the US approach) then it is not necessary to calibrate the luminescent sensor. However if the partial pressure of oxygen at 100% sat is allowed to vary depending on the local atmospheric pressure, then daily calibration will be needed to accommodate for normal pressure changes.

No change of membrane or electrolyte is required for an LDO method; the electrolyte, electrodes and membrane are replaced by the oxygen-sensitive coating on the sensor cap. All that the user has to do is change this cap about every two years depending on usage and sample matrix. Significantly lower maintenance is required for the LDO than the electrochemical techniques

The ASTM 2005 standard test method for dissolved oxygen in water includes an LDO method (ASTM 2005 [25]).

5.1.3.3 Photometric methods

Photometric test-kits are available for the determination of dissolved oxygen in aqueous solutions. These use the self-filling ampoule technology and employ rhodazine D or indigo carmine chemistries and some low level kits can detect as little as approximately 2 µg/L oxygen, whilst some high level kits will work up to approximately 40 mg/L oxygen. This information is available on the relevant manufacturers' websites

5.1.4 Reagents

5.1.4.1 *Distilled or de-ionized water*, (see **2.7.1**).

5.1.4.2 *Oxygen-free water*, for checking the zero point of the instrument. 50 g ± 1 g of sodium sulfite ($Na_2SO_3.7H_2O$) dissolved in 1 000 mL of water and 0.025 g of cobalt chloride ($CoCl_2$) dissolved in 10 mL of water. These two solutions are combined and the solution mixed. The solution is stable for about two months in a stoppered bottle.

5.1.5 Apparatus

5.1.5.1 *Dissolved oxygen meter*, comprising the following:

a) measuring probe consisting of a galvanic or a polarographic electrochemical cell encased in a gas permeable membrane, or a LDO;

b) transmitter for measuring the response of the measuring probe and providing an analogue or preferably digital display of dissolved oxygen as concentration and/or percentage saturation. The transmitter can be either single range or multi-range. For ease of use, on-site instruments preferably incorporate automatic temperature compensation, digital display of oxygen concentration and, where relevant, different concentration ranges appropriate to local requirements. Where necessary, meters which automatically compensate for salinity are recommended for routine testing.

5.1.5.2 *Thermometer*, 0 °C to 60 °C range, graduated in 0.5 °C steps, conforming to type C of BS 1704:1985 (required where the dissolved oxygen meter does not incorporate temperature compensation).

5.1.6 Samples and sampling

On-site measurements should always be taken in situ wherever possible, especially for water with depleted or supersaturated oxygen concentrations which will easily reaerate or deaerate if sampled.

Samples should not be stored for subsequent analysis by a dissolved oxygen meter. Where it is necessary to take samples for non-in situ measurement, care should be taken to minimize sample agitation during sampling and to fill the sample bottle to the top. The measurement should then be carried out as soon as possible.

5.1.7 Calibration

Calibration for most amperometric DO instruments and some luminescent-sensor instruments can only be checked with a one-point calibration at 100% saturation. For these instruments, a zero DO check should be performed routinely as an evaluation of sensor performance. Because the sensors on DO instruments might be slow to respond after the zero check, the sensor should be thoroughly rinsed with deionized water before use.

Some instruments allow for two-point calibrations at 0% and 100% saturation. Follow the manufacturer's instructions for those instruments with two-point calibration functionality. Verifying instrument performance at zero DO and using a two-point calibration can be particularly important for data accuracy when the instrument will be used to measure low DO concentrations (less than 5 mg/L).

The optical LDO method measures the oxygen concentration on the basis of a drift-free time measurement. Any wear or photobleaching of the luminophore on the sensor cap can influence the intensity but not the lifetime of the emitted red light, which is solely dependent on the oxygen concentration of the sample. All optical components are adjusted before each measurement by reference to a light pulse from the red LED, which is transmitted over exactly the same path as the emitted luminescence. Faulty calibration by the user should therefore not occur.

The manufacturer's instructions should be followed when setting up, calibrating and using the dissolved oxygen meter for testing. For on-site use, dissolved oxygen meters are normally calibrated using single-point calibration. This commonly involves setting the meter to read zero dissolved oxygen whilst immersing the measuring probe in oxygen-free water, for example reagent (**5.1.4.2**), for 2 min to 3 min and adjusting the zero reading control. For the highest accuracy, the meter should then be calibrated against air-saturated water whose dissolved oxygen concentration has been accurately analysed titrimetrically. This would normally require the test method to be calibrated within a laboratory prior to use in the on-site.

For routine testing, it is usual to air calibrate the meter with water-saturated air by placing the measuring probe loosely in a bottle containing a small amount of fresh water. The probe membrane should be wiped dry with a tissue and should not touch the water in the bottle. After leaving for at least 5 min, the meter is assumed to be at 100% saturation for the temperature and pressure of the calibration (this is the upper calibration point). It is usually assumed that the measuring probe shows a linear relationship with respect to dissolved oxygen between the zero and saturated concentration values. Where the manufacturer's instructions or recommendations differ from the above procedure, they should be followed.

*NOTE After using reagent (**5.1.4.2**), or similar zero dissolved oxygen water, to set the instrument to zero, the measuring probe should be soaked and/or well rinsed in fresh water to ensure complete removal of the reagent which would otherwise cause biased results.*

5.1.8 Procedure

Follow the manufacturer's instructions on testing procedure. Observe the following precautions.

a) Do not touch the active surface of the membrane or luminescent probe with bare fingers.

b) Soak the electrochemical measuring probes in clean water after replacing the membrane or electrolyte, or if the membrane has been allowed to dry out, until a stable reading is given.

c) Ensure that no air bubbles are trapped on the probe, or in the sampling bottle if used.

d) For electrochemical measuring probes, it is essential for the test water to flow or move past the membrane to renew the surface layer next to the membrane, which is rapidly depleted of oxygen if stationary. Even when testing a flowing body of water, gently agitate the probe within the liquid manually. Where a discrete sample is being measured, ensure vigorous movement of the probe in the sample container but avoid entraining air. This is not required for the LDO as there is no actual oxygen consumption.

e) After immersion of the measuring probe in the sample allow sufficient time for the probe to attain the water temperature and reach a stable reading. About 2 min is usually sufficient.

f) Where necessary measure the temperature of the body of water at the same time.

g) Where the sample might be of high but unknown salinity, this should be determined either on-site or subsequently unless the dissolved oxygen meter has automatic salinity compensation (see **5.1.9.2**).

5.1.9 Expression of results

5.1.9.1 Concentration in milligrams per litre or micrograms per litre of oxygen or percentage saturation

For routine on-site testing, dissolved oxygen meters fitted with automatic temperature compensation will give the concentration of dissolved oxygen or the observed percentage saturation directly. Typically, small differences of pressure from standard atmospheric pressure and the salinity effect for low salinity waters have only a small effect and are usually ignored for routine testing. The test result should be quoted to the first decimal place.

Test results from meters without automatic temperature compensation need correction if the test reading is made at a temperature different to the temperature at which the meter was calibrated (see BS EN 25814 or the manufacturer's conversion tables where supplied).

5.1.9.2 Salinity effect

Increased salinity decreases the solubility of oxygen and a saline water gives an enhanced result when measured on a meter calibrated with pure water. Corrections need to be subtracted from the observed oxygen concentration for each degree of salinity, expressed as grams

per kilogram of total salts in the sample. Salinity correction factor tables are available for correction of results given for saline samples (see BS EN 25814). Alternatively, conversion tables (where supplied by the manufacturer) should be used.

The salinity value should be independently measured on-site or in a laboratory. Portable meters are available which automatically correct for salt concentration up to 40% salinity. These are recommended for routine on-site measurements where waters of varying salinity, including estuarine waters, are routinely measured. Salinity is usually expressed in terms of sodium chloride concentration as are salinity correction tables. Where salinity is due to other salts the correction factor for sodium chloride salinity will not be correct.

5.1.10 Performance characteristics

The performance of dissolved oxygen meters is heavily dependent on the accuracy of calibration and the linearity of the instrument response. Additionally temperature, pressure and salinity corrections can be necessary for accurate determinations.

Detection limits of the order of 0.1 mg/L are typically quoted but such limits are dependent on equipment and measurements below 0.5 mg/L to 1.0 mg/L of dissolved oxygen require special precautions in respect of calibration, sampling and measurement. Meters are commercially available which are claimed to give accurate concentration readings at the level of micrograms per litre. Such meters should only be used in-line and, where relevant, in-line cooling of the flowing sample should be included. Accurate calibration for such low concentration levels is difficult to achieve. For routine on-site measurement of low content of dissolved oxygen, the colorimetric determination might be more suitable (see Annex B).

5.2 Determination of electrical conductivity

5.2.1 General

The method is based on BS EN 27888. Electrical conductivity is an empirical measurement and is a numerical expression of the ability of an aqueous solution to conduct electricity. Electrical conductivity, besides being an important physical determinand, is also commonly used as a rapid method for estimation of total dissolved ionized substances in the sample (see **5.4**).

The unit of measurement used in this test method is the SI unit millisiemens per metre (mS/m). Other commonly used units are microsiemens per centimetre (µS/cm) (1 mS/m = 10 µS/cm) and the older units micro-ohms per centimetre (µΩ/cm). Some older instruments are calibrated in these latter units and care should be taken to express results in the correct units, using where necessary the correct conversion factors (see note 2 in **5.2.9**). This also applies to the conversion of results to the correct reference temperature.

NOTE In the UK for natural, treated and waste waters, it is normal practice to report electrical conductivities in units of microsiemens per cm (µS/cm) (SCA 1978 [26])

5.2.2 Scope of this method

This test method is recommended as an on-site test for the determination of electrical conductivity. It is applicable to all types of waters including polluted and sea waters.

The analytical range for electrical conductivity is 0.1 mS/m to 20 000 mS/m, depending on cell construction, at 25 °C.

NOTE Gross suspended matter and oil or grease in the sample might foul the measuring electrodes causing incorrect or erratic results. It is advisable to refer to the manufacturer's instructions where cleaning becomes necessary.

5.2.3 Principle

Aqueous solutions are tested to determine electrical conductivity using an appropriate test instrument.

Electrical conductivity is a measure of the current conducted by ions present in water and is dependent on the type and concentration of the dissolved ions and the solution temperature and the viscosity of the solution. The test result is specified against temperature, typically 25 °C, but other temperatures can be specified. Measurement at 25 °C is preferred because it is easier to provide adequate temperature control at a little above the ambient temperature than rather a little below it.

The temperature coefficient of the conductivity of a water is typically 0.02 per °C. Thus, a typical water measured at 20 °C will have an electrical conductivity about 10% lower than that of the same water measured at 25 °C.

NOTE For the purposes of this method, electrical conductivity, also known as specific conductance, can be defined as the reciprocal of the resistance, measured under specified conditions between the opposite faces of a unit cube of defined dimensions, of an aqueous solution.

5.2.4 Reagents

5.2.4.1 *Distilled or de-ionized water*, (see **2.7.1**).

5.2.4.2 *Potassium chloride reference standard*, *c*(KCl), 0.1 mol/L. 7.456 g of potassium chloride, dried at 105 °C for 2 h, dissolved in water, diluted to 1 000 mL in a one-mark volumetric flask, and stored in borosilicate glass, in which the solution is stable indefinitely.

NOTE The electrical conductivity of this solution is 1 285.6 mS/cm at 25 °C.

5.2.4.3 *Potassium chloride reference standard*, *c*(KCl) = 0.001 mol/L. 10 mL of potassium chloride, c(KCl) = 0.1 mol/L (**5.2.4.2**), diluted to 1 000 mL with water in a one-mark volumetric flask. The solution is prepared as required and is stable for several days.

NOTE 1 The electrical conductivity of this solution is 141 µS/cm at 25 °C.

NOTE 2 Manufacturers might supply or specify other potassium chloride reference solutions for calibration purposes. It is advisable to follow the manufacturer's recommendations and to record the units used.

5.2.5 Apparatus

5.2.5.1 *Electrical conductivity meter*, comprising a measurement cell that is electrically linked to a transmitter.

a) *Measurement cell*, consisting of either a flow-through or dip-type probe fitted with suitable electrodes or an electrodeless (induction) type of cell.

NOTE There is a range of electrode materials available for electrical conductivity measurement as no one type of electrode is suitable for all types of water. Fuller details on electrode materials and their application areas are given in BS EN 27888.

b) *Transmitter*, to measure the response of the measurement cell, containing or immersed in the test sample, and display the response in terms of electrical conductivity. The transmitter might be a single or a multi-range instrument and might display in several different units. Many of the commercial systems have manual or automatic temperature compensation to allow results to be displayed for 25 °C rather than at the temperature of measurement.

5.2.5.2 *On-site and designated room/area testing facility meters*, for convenience of use in situ on-site, wider measurement tolerances than laboratory (designated room/area testing facility) equipment can usually be accepted and the test meter should where relevant incorporate features to aid convenience of use. These include:

a) easy portability, battery operated as relevant;

b) switchable multi-range settings appropriate to the expected range of measurement; this is particularly relevant where the conductivity range is variable and wide;

c) low maintenance measurement cell;

d) automatic temperature compensation to allow readout directly in conductivity at 25 °C;

e) automatic cell constant correction as an integral function to enable direct display of electrical conductivity at 25 °C.

NOTE Cell constant is a property of the measurement cell which is measured in reciprocal metres (m^{-1}) and is dependent on the geometry of the measurement cell. It can be calculated but in practice is normally specified by the manufacturer. Different ranges of electrical conductivity employ different cell constants. In practice most multi-range instruments are equipped with a control for varying the cell constant as appropriate to the selected range.

5.2.5.3 *Thermometer*, range 0 °C to 50 °C, graduated in 0.5 °C steps, conforming to type C of BS 1704:1985, required where the conductivity meter does not incorporate automatic temperature compensation.

5.2.6 Samples and sampling

Samples should be analysed with the minimum of delay, preferably using in-situ measurement. For high purity waters, flow-through cells are recommended to minimize absorption of gases which will modify the electrical conductivity. Where it is necessary to sample high purity waters separately, this should be done with minimum agitation to minimize absorption of gases.

5.2.7 Calibration

The conductivity meter should be set up for use in accordance with the manufacturer's instructions.

The sample measurement cell or dip probe cell should be rinsed with water and then the cell filled with, or the dip probe immersed in, the appropriate reference standard (**5.2.4.2** or **5.2.4.3**). Where the conductivity meter does not incorporate temperature compensation the temperature of the reference standard should be adjusted to 25 °C ±1 °C prior to calibration. The conductivity meter should then be adjusted to the known conductivity of the reference standard.

5.2.8 Procedure

Rinse the measurement cell or dip probe [**5.2.5.1**a)] with the sample. Then either fill the measurement cell with sample or immerse the test probe in the sample.

Where the conductivity meter incorporates manual temperature compensation, adjust the meter setting to the temperature of the test sample. Where the meter has no temperature compensation, record the temperature of the sample.

Allow the meter to reach thermal equilibrium and note the electrical conductivity reading, ensuring for multi-range instruments that the most appropriate range is selected.

NOTE 1 Where waters containing gross contamination have been measured, cell fouling might occur. It is advisable to calibrate regularly the conductivity meter against reference conductivity solutions.

NOTE 2 Meters with automatic temperature compensation might include a compensation system which is adjusted manually to suit the temperature of the sample under test. It is advisable to pay strict attention to the manufacturer's instructions when using, setting up or calibrating such meters.

NOTE 3 If the accuracy is to be maintained to within ±2%, the temperature compensation may not be extended over more than ±5 °C

NOTE 4 The measuring cell has to be rinsed after use and preferably stored in distilled water. Measuring cells should be cleaned, stored and maintained according to the manufacturer's instructions.

5.2.9 Expression of results

It is recommended that test results are expressed in millisiemens per metre, at 25 °C. Where other electrical conductivity units are used or alternative temperatures to 25 °C are required, this should be reported unambiguously in the test report. Conductivity meters with temperature compensation give a direct reading in the appropriate units. Meters which display in conductance units have to be multiplied by the cell constant to obtain the conductivity.

For meters without temperature compensation, if the conductivity reading is to be expressed at a temperature different from the temperature of the test sample (see BS EN 27888), it has to be corrected by a suitable factor. This allows for the temperature coefficient of electrical conductivity, which converts the electrical conductivity to the equivalent conductivity at 25 °C.

NOTE 1 Electrical conductivity is temperature-dependent and it is convention to express electrical conductivity at 25 °C. The factor will vary dependent on the sample but for many types of water the factor is approximately a 2% increase in conductivity per degree Celsius rise in temperature.

NOTE 2 For measurements not made at 25 °C (or the reporting temperature), it is advisable that the method of correction to 25 °C (or other reporting temperature) is recorded in addition to the actual measuring temperature.

NOTE 3 The following equivalent values apply for some of the more commonly used conductivity values. 0.1 mS/m = 1.0 μS/cm = 1.0 μΩ/cm = 0.001 mS/cm.

5.2.10 Performance characteristics

The accuracy of measurement depends on the type of test meter and the sample type. Typically, good commercial meters are capable of giving a relative standard deviation of less than 5% for conductivities above 5 mS/m at 25 °C.

5.3 Determination of pH

5.3.1 General

The method is based on BS 2690-109. An alternative procedure based on pH colour indicators is included in this standard (see **4.13**). pH provides a measure of the intensity of the acidity of a water sample. The pH of natural water varies but is typically in the range 4 pH units to 9 pH units. Waters outside this range are likely to be polluted or deliberately modified.

5.3.2 Scope of this test method

This test method is recommended as an on-site test for the determination of pH. It is applicable to potable, raw, industrial, polluted, saline and swimming pool waters and is measurable over the range 0 pH to 14 pH units.

NOTE pH values above 10 can be affected by a high sodium concentration. The "sodium error" can be eliminated or minimized using specialized electrodes with a low sodium error factor.

Oil or grease in samples can coat electrodes impairing electrode response. The electrode may be cleaned by gently wiping with a paper tissue.

*pH is affected by temperature and the effect may be compensated for at the measurement stage (see **5.3.8**).*

For high purity waters with low conductivity values normal electrodes will show a variable and erratic response. Special techniques and/or electrodes are necessary to achieve good results (SCA 1988 [27]).

5.3.3 Principle

The pH of a sample is determined by measuring the electromotive force produced by means of a cell consisting of a suitable glass electrode and a reference electrode immersed in the test sample. The

electromotive force is measured and displayed by a potentiometer calibrated in pH units.

NOTE For the purposes of this method, pH is defined as the negative logarithm to base 10 of the hydrogen ion concentration expressed in moles per litre.

5.3.4 Reagents

5.3.4.1 *Distilled or de-ionized water*, (see **2.7.1**).

5.3.4.2 *Buffer solutions*.

NOTE These are solutions of known pH which are resistant to changes in pH caused by contamination or dilution.

Commercial standard buffers are recommended for routine use. They are widely available in tablet or powder form, which require dissolution into a specified volume of distilled or de-ionized water. They are also available as ready-prepared solutions. Commercial solid buffers after preparation are stable for at least one month. The pH value varies with temperature and manufacturers typically quote the different pH values obtaining at the different temperature values. Some manufacturers offer colour-coded buffer solutions to aid identification.

5.3.5 Apparatus

5.3.5.1 *pH meter*, comprising measurement electrodes electrically linked to a meter which measures the response of the electrodes and displays the response as pH units and other units as appropriate. The meter can be either a single-range or a multi-range instrument. Depending on the intended use, the meter conforms to BS 2586. The meter is accurate and reproducible to at least 0.1 pH units with a range of 0 pH to 14 pH. For on-site use, the meter incorporates temperature compensation adjustment, preferably automatic temperature compensation and digital readout of pH. Typically portable on-site-use pH meters also incorporate temperature measurement.

5.3.5.2 *Glass electrode*, compatible with the pH meter (**5.3.5.1**). For routine work, a general-purpose electrode covering the pH range up to pH 13 is preferable. Above pH 10, specialized glass electrodes might be necessary and it is advisable to consult the pH meter manufacturer (see also BS 3145).

5.3.5.3 *Reference electrode*, of constant potential compatible with the pH meter (**5.3.5.1**) (see also BS 3145).

5.3.5.4 *Combination electrodes*, incorporating both the reference and measuring functions. These are particularly convenient for routine and on-site use, being more easily maintained in a non-laboratory situation. Electrically compatible with the pH meter (**5.3.5.1**).

5.3.5.5 *Thermometer*, range 0 °C to 60 °C, graduated in 0.5 °C steps, conforming to type C of BS 1704:1985; required where the pH meter does not incorporate a temperature readout or automatic temperature compensation.

NOTE Particular attention has to be given to the manufacturer's instructions for initially activating the electrode, storage after and between use, cleaning the electrode active surface and maintaining the electrolyte levels.

5.3.6 Samples and sampling

Samples should be analysed with minimal delay preferably using in-situ measurement. High purity waters including distillates are particularly liable to change pH on standing. Where in-situ measurement is not possible, sample containers should be filled to overflowing with minimal turbulence and immediately stoppered.

5.3.7 Calibration

Close attention should be paid to the manufacturer's instructions when setting up and calibrating the pH meter. Typically the pH meter-electrode system should be calibrated daily or before use at two pH values using buffer solutions of known pH. The buffers should differ by at least 3 pH units and preferably bracket or be close to the expected pH range of the test sample. For routine calibration purposes commercial buffers with pH values of 4.01 (0.05M potassium hydrogen phthalate) and 9.18 (0.05M sodium tetraborate) are widely used at 25 °C as are commercial ready-made solutions of exact pH values, e.g. 4.0, 7.0 and 9.0.

5.3.8 Procedure

Set up the pH meter (**5.3.5.1**) and electrodes (**5.3.5.2** to **5.3.5.4**) in accordance with the manufacturer's instructions.

Measure the temperature of the buffer solutions (**5.3.4.2**). Where the meter has a manual temperature setting set this accordingly.

Rinse the electrodes in the buffer solution and then immerse them in the lowest value buffer. Adjust the meter to the known pH value of the buffer at the measured temperature of the buffer.

Rinse the electrodes and immerse them in the second buffer. The meter should read to within 0.1 pH units of the correct pH value for the buffer. If not, adjust the meter to the correct pH and repeat the calibration steps until both the readings meet the accepted tolerance.

Rinse the sample container and electrode with sample and either immerse the electrodes in a test portion, or alternatively immerse the electrodes directly in the body of water. Gently move the electrodes until a stable reading is given, and note both the pH reading and the sample temperature.

*NOTE 1 High purity waters are poorly buffered and will give erratic readings (see note to **5.3.2**). The alternative colour indicator procedure (See Annex I) might be a more suitable test method for such samples.*

NOTE 2 The above procedure is a general procedure. The manufacturer's instructions might stipulate an alternative procedure.

5.3.9 Expression of results

As pH meters read directly in pH units, the pH value should be reported to the nearest 0.1 unit at the sample temperature to the nearest 1 °C. As pH varies with the temperature, it is necessary to quote both values when exact figures are required.

5.3.10 Performance characteristics

pH meters of reasonable quality will typically be capable of reading to within ±0.1 units of the correct pH value.

NOTE There is an increasing range of pH meters commercially available which vary very widely as to format, cost and specification. No guide can be given in this British Standard as to suitability, and selection is dependent on local requirements.

5.4 Determination of total dissolved solids

5.4.1 General

The method is based on BS EN 27888. The recognized laboratory procedure for measuring total dissolved solids involves evaporation of a known test portion to dryness at a temperature of 180 °C (SCA 1980 [28]) and weighing the residual solids. Electrical conductivity is widely used as a rapid method of estimating the concentration of total dissolved ionizable solids. The conversion factor used depends on the nature of the ionizable solids and will vary between different types of water. However, for waters from the same source or of a specific type the conversion factor remains fairly constant. For waters containing mainly mineral salts, such as natural waters, the estimated total ionizable dissolved solids and the true total dissolved solids show a reasonable agreement.

5.4.2 Scope of this method

This method is recommended as an on-site test for the determination of total dissolved solids. The method is applicable to raw and industrial waters.

The analytical range for total dissolved solids is up to 10 000 mg/L of total dissolved solids.

*NOTE See **5.2**. Non-ionizable dissolved solids do not contribute to the conductivity and are not included in the calculated total dissolved solids.*

5.4.3 Principle

The electrical conductivity, measured in accordance with **5.2**, is multiplied by an experimentally derived factor to give the concentration of total ionizable dissolved solids in milligrams per litre. For most waters, the conductivity expressed in millisiemens per metre at 25 °C is multiplied by a conversion factor which lies in the range 5.5 to 8.0. This is a much simpler and quicker test than the recognized laboratory procedure (see **5.4.1**), but less accurate.

*NOTE See note to **5.2.3**.*

5.4.4 Reagents

See **5.2.4**.

5.4.5 Apparatus

See **5.2.5**.

5.4.6 Samples and sampling

See **5.2.6**. Acidic or basic samples should first be neutralized to a phenolphthalein end-point by dropwise addition of 5% (m/m) sodium hydroxide or 5% (m/m) acetic acid as appropriate.

NOTE This eliminates the significantly high conductivities due to free hydroxyl or hydrogen ions.

The conductivity of the neutralized solution should be measured as usual and, where relevant, a correction should be applied for the dilution effect.

5.4.7 Calibration

5.4.7.1 Calibration of conductivity meter

See **5.2.7**.

5.4.7.2 Conversion factor (*f*)

Where necessary, the conversion factor should be experimentally derived in the laboratory. This involves direct comparison of the electrical conductivity with the true total dissolved solids (TDS), as determined by gravimetry, on a specimen test sample.

$$\text{conversion factor} = \frac{\text{TDS (in mg/L)}}{\text{conductivity (in } \mu\text{S/cm at 25°C)}}$$

NOTE Where an experimentally derived factor is not available, a factor can be arbitrarily selected. In this situation, biased results are probable.

5.4.8 Procedure

Measure electrical conductivity of the test sample in accordance with **5.2**, after neutralization where necessary (see **5.4.6**). Express the result in millisiemens per metre at 25 °C.

5.4.9 Expression of results

The total dissolved ionizable solids (in milligrams per litre) should be calculated from the following relationship:

$$\text{TDS} = \text{electrical conductivity} \times f$$

where:

electrical conductivity is measured in millisiemens per metre at 25 °C; and

f is the experimentally derived or arbitrarily selected conversion factor (**5.4.7.2**).

NOTE Where arbitrarily selected, 6.7 is the factor commonly used for most waters based on sodium sulfate as the ionic species. The factor used is also dependent on the units used to express electrical conductivity and the factor of 6.7 might not apply where conductivity is expressed in other units or at a different temperature.

5.4.10 Performance characteristics

The test results are empirical and where the factor *f* is arbitrarily selected, significant bias might result in comparison to the true TDS.

NOTE Commercial conductivity meters are available scaled directly in milligrams per litre of total dissolved solids. Typically, they use a fixed conversion factor but models with variable factors and including temperature compensation are also available commercially. No guide is given in this British Standard as to the suitability of such meters. However, it is advisable to check such meters using solutions of known TDS concentration.

5.5 Determination of turbidity

5.5.1 General

The method is based on BS EN ISO 7027. Turbidity is a reduction of transparency of a liquid caused by the presence of undissolved matter. It a visual effect resulting from the scatter or absorption of light by suspended and colloidal matter in the sample. It is a measure of the clarity or the lack of clarity of the water sample. It is also expression of the optical properties of a liquid that causes light rays to be scattered and absorbed rather than transmitted in straight lines through a sample. The measure is quantitative but is to some extent dependent on the instrument used.

NOTE Simple visual methods and photometric absorption methods are outlined in Annex I.

5.5.2 Scope of this method

This test method is recommended as an on-site test for the determination of turbidity by nephelometry. It is applicable to potable, raw, industrial and lightly polluted waters. It is not applicable to samples containing visible oil.

The range of measurement of turbidity is instrument dependent, typically up to 100 FTU (see **5.5.3**) without dilution, and commonly instruments are multi-range to allow measurement of low and high turbidities

NOTE The presence of natural colour in the sample could interfere but is minimized by using incident light with a wavelength greater than 800 nm.

Air bubbles trapped in the test portion interfere and should be eliminated by careful handling; heavy solids that rapidly settle also interfere and will cause erratic readings; they need to be separated by careful sample decantation prior to the test.

5.5.3 Principle

Incident light from a suitable light source is scattered by suspended and/or colloidal matter in a sample and the scattered light is measured at right angles (90°) to the incident light. The intensity of light scattered is compared with that measured for standard suspensions of formazine. The test result is expressed in terms of formazine turbidity units (FTU) or equivalent units, (see **5.5.10**). By convention, particulate matter that rapidly settles is removed by prior decantation and is not normally classed as part of the turbidity.

NOTE For the purposes of this method, turbidity can be defined as the reduction of the transparency of a liquid caused by the presence of undissolved matter.

5.5.4 Reagents

5.5.4.1 *Distilled or de-ionized water*, (see **2.7.1**).

5.5.4.2 *Blank water*, pre-filtered through a membrane filter of pore size 0.1 µm before use for samples of low turbidity.

NOTE It has been reported that pre-filtering water in the above manner might not reduce the turbidity reading and might even increase the reading.

5.5.4.3 *Hydrazine sulfate*, 1 % (*m/m*), 1.00 g of hydrazine sulfate ($N_2H_6SO_4$) dissolved in water, diluted to 100 mL in a one-mark flask and stored in a glass bottle in the dark. The solution is stable for at least 1 month.

WARNING. Hydrazine sulfate is poisonous, harmful to the environment and might be carcinogenic.

5.5.4.4 *Hexamethylenetetramine solution*, 10.0 g of hexamethylenetetramine ($C_6H_{12}N_4$) dissolved in water, diluted to 100 mL in a one-mark volumetric flask and stored in a glass bottle in the dark. The solution is stable for at least 1 month.

5.5.4.5 *Stock formazine standard*, 400 FTU. 5.0 mL of hexamethylenetetramine, (**5.5.4.4**) mixed with 5.0 mL of hydrazine sulfate (**5.5.4.3**) in a 100 mL one-mark volumetric flask and stood overnight. The solution is diluted to 100 mL with water, mixed and stored in a glass bottle in the dark. The solution is stable for at least 1 month.

5.5.4.6 *Calibration working standards*, prepared by accurate dilution of the stock formazine standard (**5.5.4.5**) with water (**5.5.4.1**). The values selected reflect the working ranges of the turbidity meter and are equal to the maximum value in order to calibrate the meter.

Typical ranges, required working standard and the dilution factor for dilution of the stock formazine standard are as follows:

Range (FTU)	Value of working standard (FTU)	Dilution factor (mL)
0 to 1	1.0	2.5 to 1 000
0 to 10	10.0	25 to 1 000
0 to 50	50.0	5 to 100
0 to 100	100	10 to 100

Working standards should be prepared as required and are stable for at least one week.

Manufacturers sometimes supply sealed stable liquid standards or solid standard devices of different opacity for their turbidity meters for calibration purposes. Such calibration standards are recommended for on-site testing purposes only after being checked against formazine standards. It is recommended that formazine standards, prepared as above, be tested at regular intervals and prior to initial use of turbidity meters. This will ensure that the manufacturer's supplied calibration standards give acceptable initial results and do not deteriorate with time.

Alternatively, proven commercially available standards can be used, such as styrene divinylbenzene bead suspensions (subject to them being verified as being equivalent to freshly prepared formazine

suspensions). These standards are indicated to be stable for a period of one year. Verification of proven commercial standards against formazine should be performed once every six months. Criteria for acceptable verification should be based on parallel triplicate testing of the proven secondary standards at five suspension levels. The objective of the verification is to prove that the measured average bias and precision of the secondary standard is fit-for-purpose.

5.5.5 Apparatus

5.5.5.1 *Turbidity meter*, being a nephelometer which comprises of:

a) *light source*, tungsten light, diodes or lasers giving preferably (incident light) monochromatic light at 860 nm wavelength; for on-site use, polychromatic light principally confined to the 800 nm to 900 nm bandwidth would be suitable for routine testing purposes, e.g. 860 nm with a bandwidth not exceeding 60 nm;

b) *scattered light*, with the aperture angle of the scattered diffused light between 20° and 30° and centred at right angles to the incident light path; and

c) *measuring cells*, made of glass.

NOTE Use of meters with alternative characteristics could lead to results being biased significantly from those of meters that conform to the recommendations. For on-site use, portable battery-operated meters are commercially available which conform to the recommendations.

5.5.6 Samples and sampling

Maintain all containers that come into contact with the sample in a scrupulously clean condition. Wash with hydrochloric acid or surfactant cleaning solution. Collect samples in thoroughly cleaned glass or plastics bottles, and carry out the determinations as soon as possible after collection. If storage is unavoidable, store the samples in a cool, dark room but for not longer than 24 h. If the samples have been stored cool, allow them to come to room temperature before measurement. Prevent contact between the sample and air, and avoid unnecessary changes in the temperature of the sample.

The sample should be shaken and any gross solids allowed to settle for a few minutes and the sample transferred to the measuring cell by decantation. Settlement of any small-sized slow-settling particulate matter should be avoided.

5.5.7 Calibration

The turbidity meter should be calibrated in accordance with the manufacturer's instructions using either the appropriate formazine working standards or the calibration standards supplied by the manufacturer (see **5.5.4.6**).

5.5.8 Procedure

Fill a measuring cell with the well-mixed sample (see **5.5.6**), ensuring that no air bubbles are entrapped.

Carry out the measurement immediately, in accordance with the manufacturer's instructions. For turbid samples exceeding the

maximum range of the turbidity meter (**5.5.5.1**), dilute the sample as appropriate with water (**5.5.4.1**), to bring the reading within the range of the turbidity meter. Record the dilution factor.

5.5.9 Expression of results

5.5.9.1 Undiluted sample

The result given by the turbidity meter should be expressed as turbidity in formazine turbidity units (FTU).

5.5.9.2 Diluted sample

The result given by the turbidity meter should be multiplied by the dilution factor and the result expressed as turbidity in FTU.

Some instruments are calibrated in alternative nephelometric turbidity units: provided the meter has been calibrated against formazine standards or commercial standards equivalent to formazine standards these units should be interchangeable with FTU; the use of FTU units is preferred, however.

5.5.10 Performance characteristics

Comparison between different instruments, even when calibrated against the same turbidity standards, might show differences for test samples. "Permanent" commercial calibration standards might cause bias which might alter with time, dependent on the stability of the standard.

5.6 Ion selective electrodes (ISEs)

5.6.1 General

An ion-selective electrode (ISE) is a transducer (sensor) which responds to the activity of a specific ion dissolved in a solution by a change in electrical potential which can be measured by a voltmeter or pH meter. The voltage is dependent on the logarithm of the ionic activity, according to the Nernst equation. The sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode. If ions can penetrate the boundary between two phases, then an electrochemical equilibrium will be reached, in which different potentials in the two phases are formed. If only one type of an ion can be exchanged between the two phases, then the potential difference formed between the phases is governed only by the activities of this target ion in these phases. When the membrane separates two solutions of different ionic activities and provided the membrane is only permeable to this single type of ion, the potential difference *E* across the membrane is described by the Nernst equation.

NOTE Further information can be found in Bailey [29]; Koryta [30], Midgley and Torrance [31].

There are a very large number of commercially available ISEs available, however although these devices can give fit-for-purpose results, many ISE parameters are subject to significant matrix effects in some water types. Also the response time and lifetime can be a problem with some electrodes. Calibration is normally considered essential for

each batch of analysis as small changes in potential might result in significant analyte concentration errors.

However, the only common ISE used for in-situ on-site measurements is the pH electrode (see **5.3**). Other ISEs have been successfully used for in-situ on-site measurements, but require experienced and highly trained operatives in order to obtain consistent fit-for-purpose results. When used by experienced users, robust ISE methods can often be developed for a range of parameters in given water matrices.

For these other ISE parameters such as ammonium (NH^{4+}) total ammonia, barium, bromide cadmium, calcium, chloride, cyanide, iodide, nitrate, perchlorate, potassium, silver, sodium, sulfide and thiocyanate. The user should discuss their requirements with the ISE supplier.

The fluoride ISE is commonly used to determine fluoride in potable waters, but the method is quite complex and it is felt that this method can only be satisfactorily carried out in a designated room/area testing facility with an experienced, suitably trained operative. Outline methods are given for this parameter in Annex H. (Haarhoff [16] and Noh and Coetzee [17]) and these two papers highlight the problems of fluoride analysis of potable waters using fluoride ISEs.

5.6.2 Types of ion-selective membrane

*COMMENTARY ON **5.6.2***
There are three main types of ion-selective membrane used for ion-selective electrodes that can be used for water analysis, described in this subclause.

5.6.2.1 Glass membranes

Glass membranes are made from an ion-exchange type of glass (silicate or chalcogenide). This type of ISE has good selectivity, but only for several single-charged cations; mainly H^+ and Na^+. Chalcogenide glass also has selectivity for double-charged metal ions, such as Pb^{2+}. The glass membrane has excellent chemical resistance and can work in very aggressive media. A very common example of this type of electrode is the pH glass electrode.

5.6.2.2 Crystalline membranes

Crystalline membranes are made from mono- or polycrystallites of a single substance. They have good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response. Selectivity of crystalline membranes can be for both cation and anion of the membrane-forming substance. An example is the fluoride-selective electrode based on LaF_3 crystals. The only common interfering ion is hydroxide (see **5.6.2.3**).

5.6.2.3 Ion exchange resin membranes

Ion-exchange resins are based on organic polymer membranes which contain a specific ion-exchange substance (resin). This is the most widespread type of ion-specific electrode. Usage of specific resins allows preparation of selective electrodes for a wide range of ions, both single-parameter or multi-parameter. These are also the most widespread electrodes with anionic selectivity. However, such electrodes have low chemical and physical durability as well as "survival time". An example is the potassium-selective electrode, based on valinomycin as an ion-exchange agent.

These electrodes are prepared from glass capillary tubing approximately 2 mm in diameter. Polyvinyl chloride is dissolved in a solvent and plasticizers (typically phthalates). In order to provide the ionic specificity, a specific ion channel or carrier is added to the solution; this allows the ion to pass through the vinyl, which prevents the passage of other ions and water.

One end of a piece of capillary tubing about an inch or two long is dipped into this solution and removed to let the vinyl solidify into a plug at that end of the tube. Using a syringe and needle, the tube is filled with salt solution from the other end, and can be stored in a bath of the salt solution for an indeterminate period. For convenience in use, the open end of the tubing is fitted through a tight O-ring into a somewhat larger diameter tubing containing the same salt solution, with a silver or platinum electrode wire inserted. New electrode tips can thus be changed very quickly by simply removing the older electrode and replacing it with a new one.

Application: in use, the electrode wire is connected to one terminal of a galvanometer or pH meter, the other terminal of which is connected to a reference electrode, and both electrodes are immersed in the solution to be tested. The passage of the ion through the vinyl via the carrier or channel creates an electrical current, which registers on the galvanometer; by calibrating against standard solutions of varying concentration, the ionic concentration in the tested solution can be estimated from the galvanometer reading.

In practice, there are several issues which affect this measurement, and different electrodes from the same batch will differ in their properties. Leakage between the vinyl and the wall of the capillary, thereby allowing passage of any ions, will cause the meter reading to show little or no change between the various calibration solutions, and requires that that electrode be discarded. Similarly, with use, the ion-sensitive channels in the vinyl appear to gradually become blocked or otherwise inactivated, causing the electrode to lose sensitivity. The response of the electrode and galvanometer is temperature sensitive, and also "drifts" over time, requiring recalibration frequently during a series of measurements; ideally at least one calibration sample before and after each test sample. On the other hand, after immersion in the solution there is a transient "settling time" which can be five minutes or even longer, before the electrode and galvanometer equilibrate to a new reading; so that timing of the reading is critical in order to find the most accurate "window" after the response has settled, but before it has drifted appreciably.

Interferences: the most serious problem limiting use of ion-selective electrodes is interference from other, undesired, ions. No ion-selective electrodes are completely ion-specific; all are sensitive to other ions having similar physical properties, to an extent which depends on the degree of similarity. Most of these interferences are weak enough to be ignored, but in some cases the electrode might actually be much more sensitive to the interfering ion than to the desired ion, requiring that the interfering ion be present only in relatively very low concentrations, or entirely absent. In practice, the relative sensitivities of each type of ion-specific electrode to various interfering ions is generally known and should be checked for each case; however, the precise degree of interference depends on many factors, preventing precise correction of readings. Instead, the calculation of the relative degree of interference from the concentration of interfering ions can

only be used as a guide to determine whether the approximate extent of the interference will allow reliable measurements, or whether the experimental conditions will need to be amended so as to reduce the effect of interfering ions. Total ionic strength adjustment buffers are sometimes used to control the ionic strength of the solution (and thus the activity coefficient of the analyte ion).

Section 6: Some designated room/area testing facility methods

6.1 General

This British Standard gives guidance on test methods for some water quality determinands for which there is a known demand for rapid on-site measurement. This section gives some general information on the water quality determinands that can only be analysed in designated room/area testing facilities.

6.2 Determination of oxidized nitrogen

This group includes nitrite, nitrate and total oxidized nitrogen (TON) defined as the sum of nitrite and nitrate. The determination of nitrate and TON are important for determining the water quality of treated waters and for water treatment process control. Satisfactory laboratory methods are available and commercial test-kits based on the laboratory methods are common. Test-kits based on alternative principles are available but are not recommended and not included in this British Standard. There are two primary systems using different principles and both have potential disadvantages making them unsuitable for on-site testing by non-chemists.

The most common test-kit system relies on quantitative reduction of nitrate ions to nitrite. The high degree of control necessary for quantitative reduction is extremely difficult to achieve outside the laboratory, giving non-identifiable and variable bias. Where powdered cadmium is used as the reducing agent, this might be hazardous.

Other systems are based on nitration, by the nitrate present, of a suitable organic molecule which is easily nitrated to generate an analogue which is measurable spectrophotometrically. The nitrification process typically requires the use of a highly concentrated acid medium and the use of such corrosive reagents for routine testing by non-chemists is not advised.

In the absence of a recommended quantitative test method, the use of test strips for semi-quantitative estimation of both nitrite and nitrate is recommended as an indication test for in-situ on-site testing. The test strips are based on the reduction/nitrite colour estimation principle and consist of a thin layer of reductant on a white plastic strip overlayed by a layer of the colour reagents. The strips are dipped into the test sample and the colour generated is compared against printed paper colour standards. The colours are reproducible but the discrimination between the colour standards is relatively wide and the test result is only semi-quantitative.

6.3 Determination of biological oxygen demand

6.3.1 General information on oxygen demand tests

Oxygen demand tests use either biochemical or chemical oxidation and employ empirical methods widely used, for legal purposes, as measurements of water pollution. Biochemical oxygen demand (BOD) is a chemical procedure for determining how rapidly biological

organisms utilize dissolved oxygen in a body of water. It is usually performed over a five-day period at 20 °C. It is used in water quality management and assessment. BOD is not an accurate quantitative test, although it is often used in the assessment of the quality of a river or an effluent. Many sewage final effluents have an official BOD discharge consent. Chemical oxidation demand tests are very dependent on close control of high temperature heating. This makes them unsuitable for in-situ testing but they are applicable in designated room/area testing facility for process control purposes. The two principal chemical oxidation test reagents are potassium dichromate and potassium permanganate.

NOTE 1 In many Scandanavian countries, a seven day BOD is used to reflect the colder rivers and to minimize weekend working from samples commencing incubation during the working week.

BOD measures the rate of oxygen uptake by micro-organisms in a sample of water or effluent at a fixed temperature (20 °C) and over a given period of time in the dark. The test generally takes place over an elapsed period of five days. There are two recognized methods for the measurement of BOD: the dilution method and the manometric method.

Most pristine rivers will have a five-day BOD below 2 mg/L. Moderately polluted rivers might have a BOD value in the range of 2 mg/L to 8 mg/L. Municipal sewage that is efficiently treated by a three stage process would have a value of about 20 mg/L. Untreated sewage varies, but is typically about 500 mg/L.

NOTE 2 BS EN 1899-1 describes BOD tests on diluted samples, BS EN 1899-2 describes BOD tests on undiluted samples.

To carry out a conventional BOD test (BS EN 1899-1, SCA 1988 [32]) using the dilution method requires a considerable amount of basic laboratory equipment, tends to be very time consuming and requires highly trained staff. It is also rather costly for small batches.

NOTE 3 Roppola et al [33, 34] have published comparison studies of different BOD tests.

6.3.2 Biological oxygen demand (BOD) using the dilution method

A very small amount of micro-organism seed is added to each sample being tested in case a sample has insufficient natural micro-organisms. This seed is conventionally generated by diluting a good quality sewage final effluent with de-ionized water. However, BOD seed inoculum tablets are commercially available. These contain a blend of specialized, freeze-dried microbial cultures in an easy-to-use capsule. These tablets are designed to provide a simple method for preparing a standard seeding solution suitable for the degradation of both industrial and municipal waste in five-day BOD analysis. Obtaining fresh samples of a good quality final effluent can be difficult for some laboratories. The BOD test is carried out by diluting the sample with nutrient water saturated with oxygen, inoculating it with a fixed aliquot of the above seed, measuring the dissolved oxygen and sealing the sample (to prevent further oxygen entering the sample). The sample is kept at 20 °C in the dark to prevent photosynthesis (and thereby the addition of oxygen) for five days, and the dissolved oxygen is measured again. The difference between the final DO and

initial DO is the BOD. The apparent BOD for the control is subtracted from the control result to provide the corrected value.

The loss of dissolved oxygen in the sample, once corrections have been made for the degree of dilution, is called the BOD_5. In most European countries, allylthiourea is also added at the start of the test to prevent oxidation of ammonia to nitrite and nitrate. Results from such tests are represented as BOD_5(ATU) and referred to as the "carbonaceous BOD". This test is normally carried out in laboratories owing to the relative complexity of the methodology and the large number of clean BOD bottles required. Some test-kit manufacturers do offer low-volume (approximately 60 mL) disposable plastic bottles for carrying out the BOD tests using the dilution method. They also supply the necessary reagents.

6.3.3 Biological oxygen demand (BOD) using manometry

The sample is kept in a sealed container fitted with a pressure sensor. A substance absorbing carbon dioxide (typically NaOH or soda lime) is added in the container above the sample level. The sample is stored in conditions identical to the dilution method. Oxygen is consumed and carbon dioxide is released. The total amount of gas, and thus the pressure, decreases because any liberated carbon dioxide is absorbed. From the drop of pressure, the associated software computes and displays the consumed quantity of oxygen. This method is also normally inhibits the oxidation of ammonia.

The main advantages of this method compared to the dilution method are:

a) simplicity; dilution of the sample is often not required;

b) direct reading of BOD value;

c) more cost effective for small batches of analysis; and

d) continuous display of BOD value at the current incubation time.

Furthermore, as the BOD measurement can be monitored continuously, a graph of its evolution can be plotted. Interpolation of several graphs on a similar water might help build an indication of the shape of the BOD versus time curve and allow an estimation of the five-days BOD after one or two day's incubation.

Since the previous edition of this standard, some very simple commercial manometric BOD determination devices have been developed. These devices are able to handle 6 to 12 samples per instrumental module. The method of use is described below.

A measured sample of sewage or wastewater is placed in the BOD bottle and the air-tight pressure-sensor bottle cap is then screwed onto the sample bottle. Above the sample is a quantity of air which contains 21% oxygen. Over a period of time micro-organisms in the sample utilize oxygen to oxidize organic matter present in the sample, and thus dissolved oxygen is consumed from the sample. The air in the closed sample bottle replenishes the utilized oxygen which results in a drop in air pressure in the sample bottle. This pressure drop is registered via piezoresistive electronic pressure sensors and is read directly as mg/L BOD. During the test period, the sample is continuously agitated by a magnetic stirring bar. Carbon dioxide is produced by the oxidation of organic matter and has to be

removed from the system so that the pressure difference observed is proportional only to the amount of oxygen used. This is accomplished by the addition of a few pellets of potassium (or sodium) hydroxide or soda lime in the seal cup.

These devices will typically allow monitoring of the BOD over the test duration so errors from over or under dilution can be minimized by monitoring the pressure drop after approximately 24 h. It is not necessary to wait five days before finding out that the sample has been inappropriately diluted

6.4 Chemical oxidation demand with dichromate

Chemical oxygen demand (COD) can be defined as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant.

The test using dichromate is well established as a reference laboratory test (see BS 6068-2.34). An extensive range of equivalent commercial test-kits is available based on a sealed tube version of the standard laboratory open reflux procedure. These commercial systems heat sealed tubes containing concentrated sulfuric acid solution to about 150 °C, generating very high internal pressures within the tubes. These severe test conditions and corrosive test reagents are potentially dangerous and such systems are not advised for routine testing by non-chemists.

6.5 Chemical oxidation with manganese(III)

Trivalent manganese, manganese(III) is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to faint pink when it reacts with organic matter. Manganese(III) COD results are measured colorimetrically, and the colour intensity increase at 510 nm is inversely proportional to the amount of COD in the sample. The digestion time is 60 min, but can be extended when samples are difficult to completely oxidize. The reagent typically has an oxidation efficiency of about 80% for standards prepared from potassium acid phthalate and domestic wastewater samples. No oxygen demand test will oxidize all organic compounds with 100% efficiency. With non-typical samples, standards can be prepared from other reference materials. Studies have shown that the manganese(III) COD procedure correlates very well to biochemical oxygen demand (BOD) and dichromate COD tests. Dichromate COD reagents contain mercury, chromium(VI) and silver. The absence of these materials in the manganese(III) COD reagent significantly minimizes the disposal cost and reduces exposure of the test operator to hazardous compounds. Inorganic materials might interfere with the manganese(III) COD reagent. Chloride is the most common interference and can be removed by sample pre-treatment with an ion exchange chloride removal cartridge. (This procedure needs to be evaluated to ensure no significant loss of COD occurs.) Ammonia also interferes with the test when present with chloride. The interference is very significant at high ammonia and chloride concentrations.

6.6 Chemical oxidation with permanganate

The use of potassium permanganate as a chemical oxidant is the basis of several laboratory reference procedures but there are no known equivalent commercial test-kits available. The procedure defined in BS EN ISO 8467 is widely used and is a rapid simple test that can easily be modified or adapted for on-site control testing.

6.7 Total organic carbon

Total organic carbon (TOC) testing is important in drinking water treatment as an indicator of potential disinfection by-product formation by reaction with added chlorine used to disinfect the water. In wastewater, TOC is valuable as a surrogate for COD testing and has applications in domestic wastewater pre-treatment standards, effluent discharge limitations and industrial process waters.

Until recently, this test could only be carried out in a laboratory using relatively high cost, high or low temperature TOC analysers. Both methods initially pre-treated the sample to remove the inorganic (bicarbonate) carbon by acidification to a pH < 2 and sparging. The high temperature systems then used combustion in an oxygen atmosphere at 800 °C to 1 000 °C followed by infrared detection of the liberated carbon dioxide. The low temperature systems then used acidic potassium persulfate oxidation at approximately 105 °C followed by infrared detection of the liberated carbon dioxide or by allowing the liberated carbon dioxide to diffuse through a gas permeable membrane into pure water and monitoring the change in electrical conductivity.

The TOC is determined by first sparging the sample under slightly acidic conditions to remove the inorganic carbon. Organic carbon in the sample is digested by persulfate and acid for approximately two hours at 105 °C to form carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent in an inner ampoule. The adsorption of carbon dioxide into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the colour. The amount of colour change is related to the original amount of organic carbon present in the sample.

High concentrations of bicarbonate (alkalinity) can cause breakthrough of inorganic carbon and efforts should be made to ensure that breakthrough of inorganic carbon does not occur. This can be checked by determining the sample alkalinity and then running a pure sodium bicarbonate solution of the same alkalinity concentration as the sample. This should give an insignificant total organic carbon result.

High concentrations of chloride can cause interference owing to the liberation of chlorine.

The conversion of the vast majority of soluble organic carbon to carbon dioxide is effectively quantitative. However the conversion of particulate organic carbon might be incomplete and users need to consider this when using this type of test. It is also a problem with conventional high cost instrumental TOC analysers.

6.8 Total nitrogen

Total nitrogen is the combination of organic nitrogen and inorganic nitrogen (ammonia, nitrite and nitrate). Organic nitrogen includes such natural materials as proteins, peptides, nucleic acids, urea, and numerous synthetic organic materials. Total nitrogen methods can be used to measure nitrogen loads on influent streams, at intermediate stages of water/sewage treatment to gauge overall treatment plant efficiency. Assessing nitrogen levels allows process monitoring, adjustment, and nitrogen reduction efficiency throughout the treatment.

The sample is first digested with sodium hydroxide and potassium persulfate for one hour at 100 °C, which converts all forms of nitrogen in the sample to nitrate. After the digestion is complete, a reductant is added to reduce the excess oxidant present. The nitrate is then determined by a conventional photometric method.

6.9 Determination of metals

Test methods for selected metal determinands, important for water treatment or pollution measurement, are included in this British Standard, based on colorimetric measurement. Test-kits based on colorimetric measurement are commercially available for many other metal determinands. Historically most metals were measured colorimetrically in laboratories but colorimetry has been almost universally replaced by instrumental methods for simplicity and greater specificity. Where of local interest, for on-site testing purposes, the determination of metals not included in this British Standard might often be suitably achieved using commercial test-kits, although such kits only measure available (soluble and readily solubilized metal forms), and laboratory facilities are required for determination of the total metal content. Their application is a local decision and no further guidance is given in this British Standard. It is advisable to carry out investigations, preferably by comparison against laboratory reference procedures, to investigate such factors as sample pre-treatment requirements, interferences and recoveries on suitable test samples prior to employing commercial test-kits. Reference should be made to commercial manufacturers' test-kit lists for availability and detailed information.

6.10 Determination of organic compounds

6.10.1 General

Until recently, there has been little demand for test-kits capable of determining, qualitatively or quantitatively, specific organic compounds or groups of compounds.

6.10.2 Determination of pesticides

Recent legislation has set mandatory levels for pesticides in potable water and future legislation to define limits for raw and waste waters is likely.

Laboratory analysis typically demands complex sensitive instrumental analysis, which is expensive in terms of instruments and specialized staff and is frequently very time-consuming. Such testing cannot be employed for in-situ testing.

Test-kits for qualitative and quantitative assay of pesticides are now marketed which are relatively simple to use but require an experienced person to obtain fit-for-purpose results. They employ an enzyme-linked immunosorbent assay (ELISA) technique widely used in clinical laboratories for many years for analysis of hormones and drugs. This technique uses specific antibodies for different organic molecules and is both highly sensitive and specific for individual pesticides and their related chemical groups. The test-kits are suitable as both a screening test and for quantitative assay in designated room/area testing facility test. The range of determinands is increasing rapidly. The cost per test is relatively high and a suitable QA/QC routine should be employed.

Annex A (informative) Guidance on training, supervision and associated needs

A.1 Items to be in place/actions to be taken before training

The following have to be in place or happen before training can start:

a) A suitable person experienced in using the test-kit; with a good theoretical understanding of the basis of the test-kit, able to train others in its use and competently answer any technical questions concerning the test-kit.

b) A fully documented approved test-kit method including sampling and any sample pre-treatment step.

c) Instruction on all potential hazards of the test method.

d) Instructions on safe working procedures, personal protection (PPE) equipment for the test method and the test location.

e) Instruction in the use of all test equipment used in the test method.

f) Instruction and practical demonstration of the test procedure by the trainer.

g) Supervised use of the test procedure by the test operator including, where possible, test analysis of known standards and a relevant water sample with no or a low level of analyte present and two spiked with 10% and 90% of the test-kit calibration range to demonstrate the ability of the trainee to use the test procedure correctly and achieve acceptable results.

h) A colour-vision acuity test. This should be carried out if any visual measurements are to be carried out. Unless a test operator can demonstrate acceptable colour discrimination for any visual-colour comparison-test method, the operator cannot use that particular test-kit.

A.2 On-going considerations

The QWA/QC data should be regularly inpected. If on-going QA/QC indicates a significant deterioration of operator performance, then fully documented re-training should be carried out.

On-going periodic supervision of trained personnel by an experienced person is generally considered essential for maintaining the acceptability of test results. Supervision includes occasional tests by the test operator on real samples which are then replicated by the experienced person. Where personal supervision is not available, suitable unknown check standards and a blank is supplied to the test operator on a regular basis to check the operator's performance. The check test results are reported to an experienced person as part of the on-going supervision. Such test results act as an on-going calibration check on both the test-kit and the test operator.

All training given and any subsequent re-training is documented on a suitable training record which is signed off by an experienced person. This clearly indicates that the trainee has been assessed as fit to carry out the test.

A.3 Approval of trainee

Training is subject to objective assessment against preset criteria by a competent person. The final approval lies with the trainer.

Annex B (informative) Example of a documented test-kit method and associated sampling protocol for a colorimetric method

B.1 [*determinand, e.g. aluminium*]

B.1.1 General

Determination of [the parameter of interest (*POI*), e.g. aluminium].

The method employs commercial photometric test-kit based on the analytical principle defined in a reference method. Suitable commercial test-kits based on this principle are available from a number of manufacturers.

B.1.2 Scope of this method

This test method is suitable as an on-site test for the determination of the available *POI*. It is applicable to potable, raw, industrial, lightly polluted and swimming pool waters. This method determines only soluble available reactive *POI*. Strongly complexed or insoluble *POI* is not measured.

The analytical range for a given *POI* visual test-kit is defined by the calibrated colour disc provided with the selected test-kit (see **2.5.2**).

NOTE Known interferences identified in the reference method affect test-kit methods based on the same principle.

Iron and manganese are commonly present in many water samples (especially raw waters) as potential interferences. They can often be masked by the addition of ascorbic acid, which is commonly included in some pre-packaged reagents.

Pre-packaged reagents supplied with the selected test-kit might incorporate additional reagents for suppressing known major interferences. For routine on-site testing, the potential effect of interferences are always to be taken into consideration and reported upon.

B.1.3 Principle

The sample is taken and an appropriate amount transferred into the reaction vessel. The colour-forming reagent reacts with soluble, reactive *POI* in solutions buffered to a suitable pH (*SpH*) to produce a coloured complex (*CC*) with a maximum absorption at about (λ) in nanometres. The intensity of the developed colour is measured by visual comparison or the absorbance of the solution is measured photometrically and is proportional to the concentration of reactive *POI* present.

B.1.4 Reagents

B.1.4.1 Distilled or de-ionized water

See **2.7.1**.

B.1.4.2 Pre-packaged reagents

See **2.5.2.2**.

Test-kit reagents supplied by the test-kit manufacturer are to be used. Reagents are to be stored and used in accordance with the manufacturer's instructions.

B.1.4.3 Stock standard solution, 100 mg/L of the POI

This is to be prepared on a suitable frequency basis.

This solution is normally prepared as required or supplied by the test-kit manufacturer. Many metal or metalloid standard solutions are commercially available, mainly for various atomic spectroscopic techniques, but usually have an acid matrix and because of this might be unsuitable as a test-kit standard. Some commercial chemical suppliers also provide water (rather than acid-based) 1 000 mg/L solutions of many metals, metalloids and anions.

B.1.4.4 Working standard solution

The stock standard (**B.1.4.3**) is diluted with water, using serial dilutions as appropriate, to provide suitable working standards. Working standards are prepared as required and discarded after use.

NOTE A suitable working standard will have a concentration around the mid-point of the usable calibration range of the colour disc.

B.1.5 Apparatus

NOTE An ampoule colour comparator could also be used instead of the disc comparator/disc, or portable photometer.

B.1.5.1 *Colour disc comparator or portable photometer*, (typically 350 nm to 800 nm wavelength range), as supplied with the test-kit.

B.1.5.2 *Calibrated colour disc*, which covers the calibration range between 0 mg/L and about the maximum expected concentration of the *POI*, with acceptable discrimination for intermediate concentrations.

NOTE Some manufacturers additionally include a more extended concentration range, but with possibly relatively poor discrimination, and consequentially, less accuracy.

Use of the extended, higher concentration range should be undertaken with caution and results reported accordingly, e.g. "high concentration disc used, 2 mg/L to 20 mg/L scale, ±1 mg/L".

B.1.5.3 *Test cuvettes*, appropriate to the test method, supplied with the test-kit.

B.1.5.4 *Stopwatch*, capable of reading in seconds.

B.1.5.5 *Thermometer*, range 0 °C to 60 °C, graduated in 0.5 °C steps, conforming to type C of BS 1704:1985.

B.1.5.6 Sampling protocol (drinking water sample), sample pre-treatment and preservation

NOTE For some designated room/area testing facility tests.

The tap is flushed by running it steadily for a minimum of two minutes and until at least three times the volume of water contained in the pipe connecting the tap to the water main has been passed The tap is not run at maximum flow. The sample bottle is filled with care.

Samples are analysed with a minimum of delay after sampling and are not stored for subsequent testing.

NOTE For other sample types (e.g. raw untreated waters) turbid samples are clarified by settlement or filtration prior to testing as necessary. Any sample pre-treatment protocol needs to be reported with the result.

Samples are collected in clean, polyethylene or PET (polyethylene terephthalate) bottles.

B.1.5.7 Procedure

Measure the temperature of the test sample using the thermometer (**B.3.1.5.5**) and adjust if necessary to within the tolerances specified in the test-kit manufacturer's instructions.

If the concentration of the *POI* in the test sample exceeds the maximum in the range, dilute with distilled water (**B.1.4.1**) as necessary and record the dilution factor.

Alternatively, use a system encompassing an extended range of concentrations.

Avoid dilution factors greater than 10 for on site testing purposes in order to minimize error and maintain test simplicity.

Follow the manufacturer's test-kit instructions.

Insert the *POI* test-kit colour disc (**B.1.5.2**) into the disc comparator or photometer (**B.1.5.1**). Place the test-kit cuvette (**B.1.5.3**) containing the coloured-up sample, and a matching test blank cuvette, containing untreated test sample or pre-diluted test sample as appropriate, into the comparator cell holder or use this as a blank solution for the photometer. Visually match the colour density developed in the sample against the calibrated disc standards, as viewed through the test blank solution. The concentration of *POI* in the test sample or pre-diluted sample is equivalent to the concentration value displayed on the matching calibration disc standard.

NOTE Calibration is not required due to the use of a pre-calibrated colour disc or pre-calibrated photometer method in the memory of the photometer.

Undertake a regular test using the working standard solution (**B.1.4.4**) to check the colour standards and test reagents.

Also check the test operator's ability to achieve acceptable visual colour discrimination, using appropriate working standard solutions.

B.1.5.8 Expression of results

B.1.5.8.1 Test sample

The concentration of the *POI* in milligrams per litre is read directly from the calibrated colour disc or estimated if falling between two concentration values on the disc, etc.

B.1.5.8.2 Pre-diluted sample

If appropriate, the concentration of the *POI* in the test sample is calculated by multiplying the calibrated disc reading by the dilution factor.

B.1.5.9 Performance characteristics

Meaningful comparative performance data are not obtainable.

*COMMENTARY ON **B.1.5.9***
*See commentary on Section **4**.*

The suitability of the test-kit method for specific sample matrices can be established by comparative analysis of test samples and spiked test samples using the reference method and the test-kit method under laboratory conditions.

NOTE Alternative test procedures consist of alternative comparator test-kits (see Annex I) and portable photometer test-kits (see Annex I) are also likely to be available.

Annex C (informative) Typical expected result confidence intervals from a given QC solution, from a range of test-kits from two manufacturers

Table C.1 **Typical expected result confidence intervals from a given QC solution, from a range of test-kits from two manufacturers**

Parameter	Concentration	Manufacturer	Confidence interval
	mg/L		± mg/L
Ammonium (as N)	4.00	A	0.25
Chloride	25	A	6
COD	80	A	12
COD	750	A	75
Iron	1.00	A	0.15
Nitrate (as N)	9.00	A	0.9
Orthophosphate (as P)	0.80	A	0.08
Orthophosphate (as P)	8.00	A	0.7
Sulfate (as SO_4)	100	A	15
Sulfate (as SO_4)	500	A	75
Ammonium (as N)	3.00	B	0.3
Chloride	20	B	3
COD	114	B	11
COD	400	B	40
Fluoride	1.00	B	0.2
Iron	0.10	B	0.02
Iron	1.00	B	0.2
Nitrate (as N)	6.00	B	0.8
Orthophosphate (as P)	0.63	B	0.07
Orthophosphate (as P)	25	B	3
Sulfate (as SO_4)	80	B	10

Annex D (informative) An example of target test-kit requirements for a COD test-kit used in a designated room/area testing facility

Table D.1 **An example of target test-kit requirements**

Criterion	Target specification
Unambiguous parameter definition:	Chemical Oxygen Demand (COD)
On-site or designated test room/area?	Not suitable for on-site use.
Objective of the determination:	To determine if the sample taken meets the COD requirements of the Urban Wastewater Directive (91/271/EEC). See also Dixon and Gardner (1997) for performance requirements.
Brief method summary:	Sealed tube potassium dichromate, sulfuric acid digestion at 150 °C for 2 hours with mercury sulfate suppression of chloride interference. Photometric determination of residual chromium(VI) at 440 nm.
Total/available/filtered:	Total only.
Matrices to be tested:	Sewage final effluents.
Sampling considerations	
Type of sample (spot or composite) and basic sampling protocol:	A representative spot sample from a point in the final effluent discharge channel where full mixing has taken place at the agreed times/dates and location. A documented approved sampling and sub-sampling procedure is included in the method.
Sample bottle, preservative and maximum storage time at 5 °C ±3 °C:	A one litre PET bottle with no sample preservative. Totally immerse the bottle and fill bottle to top. Analyse within 24 h.
Is sample preservation/needed?	No, if stored in a full sample bottle at 5 °C ±3 °C in the dark for up to 24 h.
Is sample pre-treatment needed?	The sample is shaken well, immediately prior to sub-sampling to ensure all suspended solids are thoroughly dispersed.
Method and QA/QC considerations	
Documented test-kit method:	A fully documented test-kit method approved by an experienced chemist is available that can meet the performance data of BS ISO 15705.
Calibration range and units:	0 mg/L – 150 mg/L
Limit of detection for typical samples and units:	< 20 mg/L
Regulatory or critical concentration value and units:	125 mg/L
Maximum tolerable total error:	20 mg/L or 20% whichever is the greater.
Maximum tolerable random error expressed as total standard deviation (% RSD) for typical samples:	5 mg/L or 5% whichever is the greater.

Table D.1 **An example of target test-kit requirements** *(continued)*

Criterion	Target specification
Maximum permitted bias for all relevant matrices:	10 mg/L or 10% whichever is the greater. An acetate (as sodium acetate) solution with theoretical COD of 125 mg/L is expected to give a COD result of greater than 112 mg/L.
Is an operator visual acuity test required for this parameter?	No.
Calibration graph r^2-value five-point graph including blank:	$\geqslant$ 0.990
Maximum blank value:	12 mg/L
Key interferences to be assessed:	Chloride (as NaCl) at 1 000 mg/L spiked into a blank and a 125 mg/L COD standard. Result is expected to be less than 12 mg/L COD positive bias.
QC solutions:	Blank, 125 mg/L COD
System suitability checks (SSCs):	Heating block temperature 145°C – 155 °C Sample 2 mL pipette tolerance 2 mL ±0.01 mL. Photometer wavelength/absorbance check.
Other considerations	
Training issues:	A documented training and re-training protocol is available.
Key health and safety considerations to be taken into account:	Very hazardous toxic and corrosive chemicals [sulfuric acid, mercury (II) chloride, chromium (VI) and silver (I)]. All used, sealed COD tubes to be returned to manufacturer for recycling. Safety visor, gloves and eyewash bottle are considered essential. The manufacturer's test-kit health and safety instructions are to be closely followed.
The target test-kit requirements are considered to be fit-for-purpose for the intended application:	YES/NO Signed Data end user name (PRINT) Organization Date

Annex E (informative) An example of target test-kit requirements for a free and total chlorine test-kit used on-site at the sampling location

Table E.1 **Example of target test-kit requirements for a free and total chlorine test-kit**

Criterion	**Target Specification** *NOTE This will vary from parameter to parameter and user to user*
Unambiguous parameter definition	Free and total chlorine. Free chlorine is defined as the concentration of residual chlorine in water present as dissolved gas (Cl_2), hypochlorous acid (HOCl), and/or hypochlorite ion (OCl-) Total chlorine is the sum of free and combined chlorine Combined chlorine is defined as the residual chlorine existing in water in chemical combination with ammonia or organic amines
On-site or dedicated test room/area?	On-site test. Both parameters are very unstable and need to be measured on-site.
Objective of the determination	To determine if both the free and total chlorine concentrations in treated final potable water are within specified limits. See also DWI [12] for performance requirements and SCA 2008 Chemical disinfecting agents in waters and effluents 2008 for background to this test
Brief method summary	DPD test for free chlorine and DPD test with excess KI for total chlorine with photometric determination at 520 nm of both parameters
Total/available/filtered	Total
Matrices to be tested	Potable water within relevant distribution systems
Sampling considerations	
Type of sample (spot or composite) and basic sampling protocol	Spot sample. The tap should be flushed by running it steadily for a minimum of two minutes and until at least three times the volume of water contained in the pipe connecting the tap to the water main has been passed. The tap should not be run at maximum flow. A documented approved sampling procedure is included in the method.
Sample bottle, preservative and maximum storage time at 5 °C ±3 °C	Collect sample from the relevant tap in the test-kit cuvette as per documented method. Analyse within 5 min of taking sample.
Is sample preservation/ needed?	No. Not possible for these two parameters
Is sample pre-treatment needed?	No.

Table E.1 **Example of target test-kit requirements for a free and total chlorine test-kit** *(continued)*

Criterion	Target Specification *NOTE This will vary from parameter to parameter and user to user*
Method and QA/QC considerations	
Documented test-kit method	A fully documented test-kit method with manufacturer's performance data approved by an experienced chemist is available
Calibration range and units	0 mg/L – 2 mg/L
Limit of detection for typical samples (4.65 s) and units	< 0.05 mg/L
Regulatory or critical concentration value and units	Water company specified. Sample point specific.
Precision expressed as % RSD for a typical sample matrix	< 5% or less than 0.025 mg/L whichever is the greater
Maximum permitted bias for all relevant matrices	±10% or less 0.05 mg/L whichever is the greater.
Is a visual acuity test required for this parameter?	No
Calibration graph r^2 value five point graph including blank	$\geqslant$ 0.990 using KMnO4 (See SSC below)
Maximum blank value	0.05 mg/L
Key interferences to be assessed	None. Well established and proven test method for potable waters
QC solutions	On a regular basis, the test-kit operator should run a chlorine AQC of a randomized blank, approximately 0.1 mg/L and 0.4 mg/L free chlorine standard in a dedicated test room/ area prepared by an experienced person. Fully traceable stable standards, containing 20 mg/L to 50 mg/L chlorine, in sealed glass vials are available for this purpose
System suitability checks (SSCs)	Blank < 0.05 mg/L. Check standard gel cuvette supplied with test-kit or a fresh (up to 24 hour) to check photometer response of a 0.891 mg/L solution of $KMnO_4$ is equivalent to 1 mg/L free chlorine
Other comments	If the sample were to contain more than 5 mg/L free chlorine, then the red colour normally produced could be completely bleached. If a transient red colour is ever observed, then dilute the sample 10 times with RO/DI water and repeat the analysis.

Table E.1 **Example of target test-kit requirements for a free and total chlorine test-kit** *(continued)*

Criterion	**Target Specification** *NOTE This will vary from parameter to parameter and user to user*
Other considerations	
Training issues	A documented training and re-training protocol is available
Key health and safety considerations to be taken into account	Follow manufacturer test-kit health and safety instructions
The target test-kit requirements are considered to be fit-for-purpose for the intended application	YES/NO Signed Data end user name (PRINT) Organization Date

Annex F (informative) An example of routine QA/QC documentation for a COD test

Table F.1 **COD test on-going method performance data**

Designated room/area testing facility parameter	**Month and year**						
COD	**Nov-07**						
				Result			
Criterion	**Target**	**Date**	1 →	2	3	4	5 →
SSC1 Block temperature	145 °C – 155 °C		147	150	149	152	144[A)] 150
SSC2 Sample pipette volume check	2 mL ±0.01 mL		2.005	2.003	1.998	1.995	2.004
SSC3 Photometer absorbance check with $K_2Cr_2O_7$ standard	0.400 ±0.008		0.405	0.402	0.398	0.404	0.400
Blank (at start and then every 20 samples in batch)	< 12 mg/L		< 12	< 12	< 12	< 12	< 12
125 mg/L standard (at start and then every 20 samples in batch)	125 mg/L ±12.5 mg/L		123	110[B)] 123	130	119	122
1 000 mg/L chloride (as NaCl)	< 12 mg/L		< 12	< 12	< 12	< 12	< 12
Comments including reference to remedial actions		[A)] Block temp adjusted [B)] Fresh AQC solution prepared					
SSC = system suitability check							

Annex G (informative) An example of routine QA/QC documentation for a free and total chlorine test

Table G.1 **Free and total chlorine test**

Designated room/area testing facility parameter	**Month and year**						
COD	**Nov-07**						
			Result				
Criterion	**Target**	**Date**	1 →	2	3	4	5 →
SSC1 0.891 mg/L KMnO4 solution result (equivalent to 1 mg/L free chlorine)	0.9 mg/L – 1.1 mg/L free chlorine		0.95	0.88[A)] 0.96	1.04	1.07	0.95
SSC2 Photometer check 1 mg/L sample gel standard	0.9 mg/L – 1.1 mg/L free chlorine		0.92	0.98	1.02	1.08	0.96
Blank (at start and then every 20 samples in batch)	< 0.025 mg/L		< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Weekly QC error check in designated room/area testing facility of unknown standards for free and total chlorine prepared by an experienced person	Within 10% of nominal value		-8.5%				
Comments including reference to remedial actions		[A)] Scratched cell replaced					
SSC = system suitability check							

Annex H (informative) An example of a typical Shewhart control chart and a blank Shewhart control chart

Figure H.1 shows a typical example of an analysis method under control with statistically-determined warning and action limits.

Figure H.2 shows a blank control chart. The action limit values on the QC chart for test-kits will often be fixed action limits agreed with the result end user rather than statistically derived from the method validation data. This is considered adequate for test-kit usage for many simple applications, but might not be sufficient when the value of the result is critical. Arbitrary warning limits can also be set up for simple applications if required.

Figure H.1 **Example Shewart control chart**

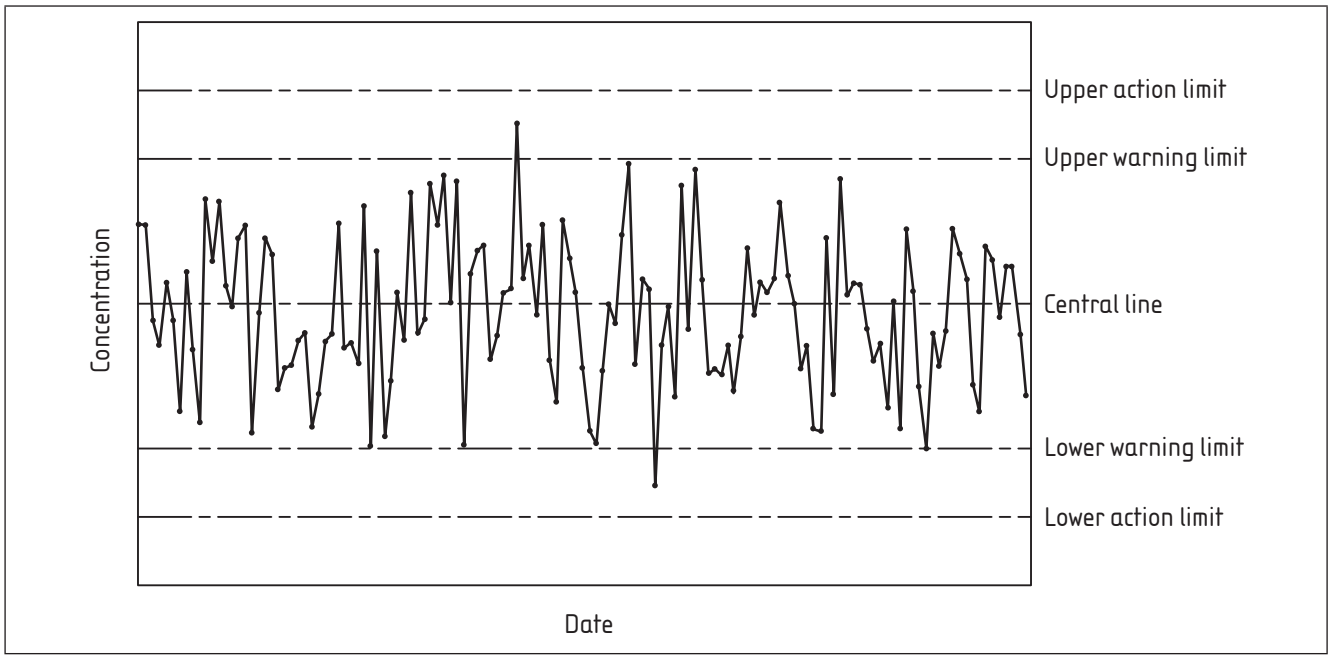

Figure H.2 **Blank Shewart control chart**

Annex I (informative) Test-kit methods overview

Photometric or visual methods for use on-site or in a designated room/area testing facility	
Aluminium	Magnesium
Ammoniacal nitrogen	Manganese
Ascorbic acid	Mercaptobenzothiazole (MBT)
ATP	Methanol
Biocides	Molybdate
Boron	Nitrogen (total)
Bromine (as total residual bromine)	Nickel
Cadmium	Oil
Chlorine (free and total)	Organic acids
Chlorine dioxide	Organophosphonate compounds
Chromium(VI)	Oxygen (dissolved) µg/L
Cobalt	Oxygen (dissolved) mg/L
Colour	Ozone
Copper	Peracetic acid
Complexing agents	pH
Cyanide free	Phenols
Cyanuric acid	Phosphate (Low range)
Detergents (anionic)	Phosphate (High range)
Detergents (cationic)	Silica
Detergents (non-ionic)	Phosphonate
Dissolved oxygen (photometric)	Quaternary ammonium compounds (QACs)
DEHA diethylhydroxylamine	Silica
Fatty acids	Silver
Filming amines	Sludge activity by means of the dehydrogenase activity using 2,3,5-triphenyltetrazoliumchloride (TTC)
Fluoride	Sulfate
Formaldeyde	Sulfide
Glutaraldehyde	Sulfite
Glycol	Tannins
Hydrazine	Thiocyanate
Hydrogen peroxide	Tin
Iron(II)	Thiocyanate
Iron total	Zinc
Iron (soluble and total)	
Lead	

Designated room/area testing facility methods with photometric endpoint	
Adsorbable organic halides (AOX)	Permanganate value (PV)
Biological oxygen demand (BOD)	Total organic carbon (TOC)
Chemical oxygen demand (COD)	Total nitrogen
Chlorine demand	Total phosphorus
Microbial dehydogenase activity	
Titration test-kit methods for use in on-site or in a designated room/area testing facility	
Alkalinity	Nitrite
Calcium and total hardness	Sulfate
Chloride	Sulfite
Free carbon dioxide	
Instrumental methods for use on-site or in a designated room/area testing facility	
Dissolved oxygen	Redox methods
Electrical conductivity	Total dissolved solids
Electrochemical methods	Turbidity
pH	UV diode array
Other methods including screening methods (mainly for use in designated room/area testing facilities)	
Biotoxicity simple tests	Organics including pesticides and herbicides
ELISA based test-kits	Screening analysis

Annex J (informative) Summary of test-kits

J.1 General

This annex is only intended as a general guide, it is not exhaustive and it is important to note that new and improved test-kits are continually being developed. Users are advised to check test-kit manufacturers' websites for up-to-date information with respect to test-kits of interest.

Only the most sensitive range is cited in Annex J. Less sensitive ranges are usually available for most test-kits. Alternatively, manual dilution of the sample can be also be used. Automatic dilution is available in some test-kits by using a capillary tip to take up a smaller precise volume of the sample.

All concentration values given in Annex J are just indicative values. As stated above, further, updated information can be found on test-kit manufacturers' websites.

The lower measuring range limit cited might not be taken as the detection limit. The limit of detection of a given test-kit is normally very dependent upon the sample matrix. The typical lower measuring levels quoted apply to a treated drinking water. For more complex matrices the lower measuring levels might be significantly higher than those given here.

It is advisable that all users of visual test-kits should take a visual acuity test.

J.2 Test formats and sensitivity

Many conventional visual tests are carried out in 10 mm to 13 mm path-length open measuring cells. For some tests, vertical comparator cells with a much longer cell path length (up to approximately 150 mm) can be used to obtain a greater sensitivity and improved detection limits. Vacuum-sealed visual kits normally have two calibration ranges:

a) most sensitive, by viewing along the tube axis (approximately 100 mm in length);

b) less sensitive (by approximately ten times) by viewing across the tube axis.

For some tests (e.g. chlorine, hydrazine, silica and dissolved oxygen) extended length tubes (approximately 250 mm length) are available to increase the sensitivity even further.

For some conventional photometric tests the commonly used 13 mm path length open cell can be replaced by a longer path length (typically 50 mm) rectangular conventional cell to obtain a greater sensitivity and improved detection limits.

However, it is important to appreciate the use of longer path lengths is usually limited to clean waters without appreciable turbidity or background colour.

J.3 Temperature

The rate of reaction of most colorimetric methods used in test-kits is temperature dependent. Most tests need to carried out within a specified temperature range. This should be checked before using any

given test-kit. At low temperatures, significantly negatively biased results are likely to be obtained.

J.4 Summaries

J.4.1 Informative summary examples

Tables J.1 and J.2 are given as informative or background summaries of the type that might be useful for training the sampling/testing operatives or for retention at a permanent laboratory. They are actual summaries for test-kits at the time of publication.

Table J.1 **Informative summary – Aluminium**

Parameter	Aluminium
Speciation (if relevant)	Available aluminium without pre-digestion. For samples with particulate matter present where a total aluminium is required, a pre-digestion step followed by neutralization is required to determine total acid soluble aluminium. A designated room/area testing facility is needed for this.
Background information	Natural waters contain variable, but minor, amounts of aluminium, despite its universal distribution and abundance usually in highly unavailable forms. Aluminium might be present in a sample in a number of different forms (soluble, colloidal or particulate). It is important for the user of the results to define their measurement requirements.
Principle	Eriochrome cyanine R dye chelates with soluble reactive aluminium in solutions buffered to pH 6.0 to produce a red to pink coloured complex with a maximum absorption at about 535 nm. The intensity of the developed colour is measured by visual comparison and is proportional to the concentration of reactive aluminium present. A number of standard procedures based on a similar principle but using alternative chelation dyestuffs have also been published, including BS 2690-106.
Scope	Visual comparator or photometric test methods should be suitable as an on-site test for the determination of low levels of available aluminium. These methods are applicable to potable, raw, industrial, lightly polluted and swimming pool waters. The analytical range for aluminium is defined by the method. Most available test-kit methods are applicable to potable treated waters, raw, industrial, lightly polluted and swimming pool waters. Without sample pre-treatment with acid and/or addition of matrix effect suppressors, this method determines only soluble reactive aluminium. Complexed or insoluble aluminium is not measured.
Detection method	
Comparator (visual)	**Yes**
Photometric	**Yes**
Electrochemical	
Instrumental (other)	
Titrimetric	
Approx most sensitive detection limit	10 µg/L

Table J.1 **Informative summary – Aluminium** *(continued)*

Parameter	Aluminium
Interferences	Iron and manganese are commonly present interferences which can react with the colour forming reagent. They can be masked by the addition of ascorbic acid, which is commonly included in the pre-packaged reagents. Fluoride is a significant interference in fluoride-dosed drinking waters (typical fluoride concentration about 1 mg/L). Fluoride ions form a strong complex with aluminium ions and the complexed aluminium will not react quantitatively with the colour forming reagent. Most test-kits give details of a simple algorithm to correct the negatively biased aluminium result assuming the fluoride concentration is known. This will decrease the accuracy of the measurement. Polyphosphate (e.g. in polyphosphate dosed waters) interferes and needs to be hydrolysed to orthophosphate.
NOTE 1 For typical method performance data including the calibration range consult the test-kit manufacturer's literature and/or website	
NOTE 2 Aluminium is ubiquitous and great care is needed to avoid contamination when carrying out low level aluminium analysis	
NOTE 3 Without sample pre-treatment with acid and subsequent sample neutralization, this method determines only soluble reactive aluminium.	

Table J.2 **Informative summary – Iron**

Parameter	Iron
Speciation (if relevant)	Available iron(II) or available iron(II + III) without pre-digestion. For samples with particulate matter present a pre-digestion step followed by neutralization is required to determine total iron.
Background information	Natural waters contain variable, but minor, amounts of iron, despite its universal distribution and abundance usually in highly unavailable forms. Iron in ground waters is normally present in the ferrous [Fe(II)], or soluble state, which readily oxidizes to ferric [Fe(III)] iron on exposure to dissolved oxygen. Iron might be present in a sample in a number of different forms [Fe(III), Fe(II), soluble, colloidal, particulate]. It is important for the user of the results to define their measurement requirements. Test-kit manufacturers normally include a suitable reducing agent within the pre-packaged reagents to reduce iron(III) to iron(II) to enable total available iron to be measured by colorimetric methods. In practice weakly chelated and some easily solubilized particulate iron, if present, is activated during the test procedures and is included in the iron concentration found. Particulate bound iron is not measured unless a suitable acid digestion procedure is used followed by sample neutralization. This is not considered feasible for on-site measurements. Iron can enter a water system from leaching of natural deposits, iron-bearing industrial wastes, effluents of pickling operations, or from acidic mine drainage.
Principle	Colorimetric method reagents include 1,10 phenanthroline; 3-(2-pyridyl)-5, 6-bis (4-phensylsulfonic acid)-1, 2, 4-triazine (PDTS), monosodium salt; 3-(2-pyridyl)-5,6-bis (4-phenylsulfonic acid)-1,2,4-triazine disodium salt (Stookey, L.L., Anal. Chem., 42(7), 779 (1970)); 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ). All these reagents require prior reduction of iron(III) to iron(II). For total available iron in brines there is a ferric thiocyanate method with an approx LOD of 5 mg/L. High-range titration procedures are also available, such as sulfosalicylic acid indicator method with EDTA as the titrant after conversion of any iron(II) to iron(III).

Table J.2 **Informative summary – Iron** *(continued)*

Parameter	Iron
Scope	Colorimetric test methods are recommended as on site tests for the determination of low concentrations of iron(II) or total iron. These methods are applicable to potable, raw, industrial, lightly polluted and swimming pool waters. The analytical range for iron is defined by the method used. Colorimetric or titrimetric methods can be used for higher iron concentrations in waste waters and can measure total iron, iron(II) and iron(III).
Detection method	
Comparator (visual)	**Yes**
Photometric	**Yes**
Electrochemical	
Instrumental (other)	
Titrimetric	**Yes** (for higher levels).
Approx most sensitive detection limit	10 µg/L Colorimetric 10 mg/L Titrimetric
Interferences	For most waters, not thought to be very significant. Chelating agents such as EDTA cause negative bias. The same interferences will occur as found in the equivalent laboratory reference method. See test-kit manufacturer's literature for specific details of interferences.

NOTE 1 For typical method performance data including the calibration range consult the test-kit manufacturer's literature and/or website.

NOTE 2 Iron(II) is rapidly oxidized to iron(III) by dissolved oxygen. If iron speciation measurements are to be undertaken great care should be taken to minimise oxidation by avoiding any air entrainment into the sample and carrying out the measurement as soon as possible after taking the sample.

NOTE 3 Without sample pre-treatment with acid and subsequent sample neutralization, this method determines only soluble reactive iron.

J.4.2 Availability summary

Table J.3 summarizes visual and photometric test-kit availability, along with typical measuring ranges.

Table J.3 **Availability of visual and photometric test-kits**

Parameter	Designated test room test	Visual typical measuring range (mg/L) See associated notes		Photometric typical measuring range (mg/L) See associated notes		Potential main interferences	Comments
		Lower	Upper	Lower	Upper		
Aluminium	—	0.1	1	0.01	0.8	Fluoride. Polyphosphate interference can be reduced by converting polyphosphate to orthophosphate	—
Ammoniacal nitrogen	—	0.02	0.5	0.02	0.8	Salicylate method, iron, sulfide, hydrazine and glycine	Destroy any free chlorine with sodium thiosulphate on taking the sample. The Nessler mercury method uses a reagent that contains mercury
Ammoniacal nitrogen	—	0.05	0.8	0.02	2	Nessler method, iron, high total hardness, amines	
Adsorbable organic halides (AOX)	Yes	—	—	0.05	2.5	Inorganic halides especially chloride. Follow test-kit manufacturer's guidelines to minimize this interference	Solid phase extraction of organohalogens, removal of any remaining inorganic halides, oxidative digestion of the organohalogens to Cl^-, Br^- and I^- ions, photometric determination of the resulting halides. Result reported as chlorine

Table J.3 **Availability of visual and photometric test-kits** *(continued)*

Parameter	Designated test room test	Visual typical measuring range (mg/L) See associated notes		Photometric typical measuring range (mg/L) See associated notes		Potential main interferences	Comments
		Lower	Upper	Lower	Upper		
Arsenic	Yes	—	—	0	0.2	Easily reduced substances	Arsenic is reduced to arsine gas in a specially equipped distillation apparatus. The arsine is passed through a scrubber into an absorber tube containing silver diethyldithiocarbamate in pyridine. The arsenic reacts to form a red complex
Ascorbic acid, see DEHA, oxygen scavengers							
Biological oxygen demand (BOD)	Yes			2	3000	—	—
Boron	—			0.05	1	—	Typically azomethine or carminic acid methods
Bromate	—			0.003	0.15	—	Use of the standard addition method to verify results is recommended
Bromine (as total residual bromine)	—	0.1	2	0.05	5	Chlorine, chlorine dioxide, iodine	Bromine will respond to most chlorine test-kits on an equimolar basis.
Cadmium (soluble)	—			0.02	0.3	—	Cadion method
Cadmium (soluble) (extraction)	Yes			0.002	0.5	—	Dithizone method with chlorinated solvent
Carbon dioxide (free), titrimetric	—			10	1000	—	Simple titrimetric method

Table J.3 **Availability of visual and photometric test-kits** *(continued)*

Parameter	Designated test room test	Visual typical measuring range (mg/L) See associated notes		Photometric typical measuring range (mg/L) See associated notes		Potential main interferences	Comments
		Lower	Upper	Lower	Upper		
Chemical oxygen demand (COD)	Yes			2	40	Chloride above about 1 000 mg/L.	For urban wastewater treatment (UWWT) compliance analysis, the 10 mg/L – 150/160 mg/L range recommended
Chloride	—	2	20	0.2	25	Sample pH should be adjusted to pH 6 – 8 if necessary. Test also responds to bromide and iodide	Iron (III) thiocyanate method
Chlorine (free and total)	—	0.02	0.6	0.02	2	—	Most test-kits are based upon controlled reaction with DPD
Chlorine dioxide	—	0.02	0.5	0.01	1	—	Glycine is added to avoid free chlorine interference when using DPD based test-kits
Chromium total	Yes	—	—	0.01	0.7	—	—
Chromium(VI)	—	0.1	1	0.01	0.7	Iron	1,5-Diphenylcarbohydrazide method. Sample pH should be adjusted to pH 6 - 8 if necessary.
Cobalt	—			0.01	1	—	—
Colour (Hazen units)	—	5	100	0.5	50	—	—
Copper (soluble)	—	0.04	0.5	0.04	5	—	—
Cyanide free	—	0.002	0.4	0.002	0.25	Free chlorine; cobalt; nickel; thiocyanate	If thiocyanate is suspected, carry out a thiocyanate test as thiocyanate responds upon an equimolar basis as cyanide

Table J.3 **Availability of visual and photometric test-kits** *(continued)*

Parameter	Designated test room test	Visual typical measuring range (mg/L) See associated notes		Photometric typical measuring range (mg/L) See associated notes		Potential main interferences	Comments
		Lower	Upper	Lower	Upper		
Cyanuric acid	—	10	100	5	50	—	—
DEHA (diethylhydroxylamine) (Oxygen scavenger test.)	—	0.02	0.4	0.05	1	Iron(II)	Diethylhydroxylamine (DEHA) or other oxygen scavengers present in the sample react with iron(III) to produce iron(II) in an amount equivalent to the DEHA (or oxygen scavenger) concentration. The iron(II) formed is then photometrically determined. Temperature and reaction times are critical
Detergents (anionic) (extraction)	Yes	0.1	1	0.002	0.3	If a water contains cationic and anionic detergents, equivalent quantities combine and will not be detected	—
Detergents (cationic) (extraction)	Yes	1	20	0.05	2		
Detergents (non ionic) (extraction)	Yes	—	—	0.1	5	—	—
Fatty (organic) acids	Yes	—	—	30	3000	—	Expressed as acetic acid
Fluoride (soluble)	—	0.1	2	0.05	2	Aluminium	Use of the standard addition method to verify results is recommended. To determine total fluoride a pre-treatment step is required. Distil the sample (in a test room) with sulphuric acid to liberate all forms of fluoride.
Formaldehyde	—	0.1	1	0.003	1	Other aldehydes	—

Table J.3 **Availability of visual and photometric test-kits** *(continued)*

Parameter	Designated test room test	Visual typical measuring range (mg/L) See associated notes		Photometric typical measuring range (mg/L) See associated notes		Potential main interferences	Comments
		Lower	Upper	Lower	Upper		
Glycol	—	1	15	0.6	10	—	Will detect both ethylene and propylene glycols. Results normally reported as ethylene glycol.
Hydrazine	—	0.1	2	0.004	0.6	—	—
Hydrocarbons	—	—	—	0.5	5	—	Extraction with pentane, clean-up, evaporation of solvent, followed by photometric COD test to oxidize all HCs with a boiling point above 120 °C.
Hydrogen peroxide	—	0.05	0.5	0.03	2	—	—
Iron(II)	—	0.02	0.2	0.02	5	—	—
Iron total	Yes	0.02	0.2	0.02	5	—	Digestion required
Lead (extraction)	Yes	—	—	0.005	0.15	—	—
Magnesium	—	—	—	5	75	—	—
Manganese	—	0.03	0.5	0.01	0.7	—	—
Methanol	—			0.2	15	—	Enzyme reaction mechanism
Molybdate	—	1	7	0.02	1	—	—

Table J.3 **Availability of visual and photometric test-kits** *(continued)*

Parameter	Designated test room test	Visual typical measuring range (mg/L) See associated notes		Photometric typical measuring range (mg/L) See associated notes		Potential main interferences	Comments
		Lower	Upper	Lower	Upper		
Monochloramine	—	—	—	0.01	2	—	Controlled reaction with DPD. Alternative method uses a cyanoferrate catalyst, where monochloramine (NH_2Cl) in the sample reacts with a substituted phenol to form an intermediate monoimine compound which is detected photometrically.
Nitrate as NO_3^-	—	0.25	3	0.2	30	—	Some kits use cadmium (red list substance) as a reducing agent
Nitrite as NO_2^-	—	0.005	0.1	0.003	0.5	—	—
Nitrogen (total)	—	—	—	0.5	20	—	—
Nickel (soluble)	Yes	0.1	1.5	0.01	1	—	—
Organic acids, see Fatty (organic acids)	Yes	—	—	—	—	—	—
Oxygen (dissolved) mg/L (boiler feed waters)	—	0.002	0.02	0.006	0.8	—	Rhodazine D and indigo carmine methods can be used. A suitable sampling procedure is needed to monitor these low levels. See test-kit manufacturer's website
Oxygen (dissolved) mg/L, waters	—	1	10	0.5	10	—	—
Oxygen scavengers, see DEHA	—	—	—	0.003	0.45	—	—

Table J.3 **Availability of visual and photometric test-kits** *(continued)*

Parameter	Designated test room test	Visual typical measuring range (mg/L) See associated notes		Photometric typical measuring range (mg/L) See associated notes		Potential main interferences	Comments
		Lower	Upper	Lower	Upper		
Ozone	—	0.05	0.6	0.01	0.75	—	—
Peracetic acid	—	0.1	1	0.4	4	Most oxidizing agents	—
Phenols (phenol index)	—	0.1	1	0.2	5	4-aminoantipyrene	—
Phenols (extraction method)	—	—	—	0.002	0.1	—	—
Phosphate (reactive)	—	0.01	0.25	0.05	5	silicate	—
Phosphonate	Yes	—	—	0.1	2.5	—	Digestion to phosphate
Phosphorus total	Yes	—	—	0.05	5	—	—
Polyoxycarboxylic acids (POC)	—	—	—	1	40	—	—
Quaternary ammonium compounds (QACs) for cooling tower and pool/spa waters	—	1	20	0.2	5	—	—
Silica (reactive)	—	0.01	0.3	0.01	1.6	Sulfide	Contamination can be a problem
Silver (soluble)	—	—	—	0.005	0.7	—	—
Sulfate	—	25	200	5	250	—	—
Sulfide (soluble)	—	0.1	1	0.02	1.5	Thiocyanate and nitrite can interfere and cause low results	Easily oxidized during sample storage
Tannin and lignin	—	—	—	0.1	9	—	—
Thiocyanate	—	—	—	0.5	50	—	—
Tin (soluble)	—	—	—	0.1	2.5	—	—

Table J.3 **Availability of visual and photometric test-kits** *(continued)*

Parameter	Designated test room test	Visual typical measuring range (mg/L) See associated notes		Photometric typical measuring range (mg/L) See associated notes		Potential main interferences	Comments
		Lower	Upper	Lower	Upper		
Total organic carbon (TOC)	—	—	—	0.3	20	Bicarbonate	TOC is determined by first sparging the sample under acidic conditions to remove all inorganic carbon. Then the organic carbon in the sample is digested by persulfate and acid to form carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent in an inner ampoule. The adsorption of carbon dioxide into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the colour. The amount of colour change is related to the original amount of carbon present in the sample.
Zinc	—	0.25	3	0.02	3	—	—

Annex K (informative)

Indication of availability of visual test sticks for semi-quantitative determinations

*COMMENTARY ON ANNEX **K***

This annex is only intended as a general guide. It is not exhaustive and it is important to note that new and improved test sticks are continually being developed. Users are advised to check test-kit manufacturers' websites for up-to-date information with respect to test-kits of interest.

Most of the test strips respond selectively to a given ion or substance, as masking agents are added to the reaction zone to eliminate or suppress various potential interferences; interferences cannot, however, be avoided in all instances, although most test strips have been tested with a number of ions for their possible interfering effects.

NOTE 1 These are listed in interference tables compiled for the various manufacturers, often available on the test stick manufacturers' website, or supplied with the test-kit.

Test sticks allow users to perform time-saving semi-quantitative determination of a range of substances in the mg/L range without additional preparation of the samples, other than possibly a simple pH adjustment. It is important to appreciate that the results are semi-quantitative. The tests are ideal for assessing whether a given parameter is significantly below or significantly above a given concentration.

Users should carry out some simple validation checks on a range of unspiked and spiked typical samples and also compare the results against a validated quantitative method.

Only the most sensitive range is cited in this annex. For a few test sticks, less sensitive ranges are available.

All concentration values given in Annex K are just indicative values; as stated above, further and updated information can be found on test sticks manufacturers' websites.

The lower measuring range limit cited is not necessarily the detection limit. The limit of detection of a given test stick is dependent upon the sample matrix. The typical lower measuring levels cited apply to a treated drinking water, for more complex matrices the lower measuring levels might be higher than those cited.

The rate of reaction of many colorimetric methods used for test sticks is temperature dependent. Most tests need to carried out within a specified temperature range. This should be checked before using any given test sticks. At low temperatures, significantly negatively biased results are likely to be obtained.

It is recommended that all users of visual test sticks should take a visual acuity test.

NOTE 2 The arsenic test requires a simple reaction of the sample with zinc and a (solid) acid to form arsine which then reacts with a chemical on the test stick.

For most tests, the reaction zone on the test stick is wetted with the solution being tested by simple dipping. The excess liquid is then shaken off. After the given reaction time has elapsed, typically 10 s to 120 s, the colouring of the reaction zone is compared with the colour scale on the test stick container to determine the analyte concentration.

For improved quantification, more elaborate test sticks are available for a wide range of substances. These can be read by inserting the relevant side of the test strip into a portable reflectometer which can also store the results. This gives better quantification than the equivalent test strip method with visual interpretation. It also gives

improved sensitivity and the result is not influenced by the operator's visual acuity.

Reflectometric test sticks require a somewhat higher degree of operator skill than simple visual test sticks. Information on potential interfering substances is normally available on the websites of the relevant reflectometric test stick manufacturers.

As the colour of the reaction zone might continue to change after the specified reaction time has elapsed, it is very important that the colour is only monitored at the appropriate, specified time. If the colour of the reaction zone is equal to or more intense than the darkest colour on the scale, the measurement is best repeated using a fresh, suitably diluted sample. For many tests, a wide range of concentrations can be covered with a given test stick.

Table K.1 **Indication of availability of visual test sticks for semi-quantitative determinations**

Parameter	Typical measuring range (mg/L)		Comments
	Lower	Upper	
Aluminium	5	500	—
Ammoniacal nitrogen	10	400	—
Arsenic	0.005	0.5	Modified Gutzeit type test. Zinc and a solid acid are added to the sample. Arsine is liberated from the acidified sample, which then reacts with mercury(II) bromide contained in the reaction zone of the test strip to form yellow-brown mixed arsenic mercury halogenides.
Ascorbic acid	50	2 000	—
Calcium	10	100	—
Chloride	500	3 000	—
Chlorine (free and total)	0.5	20	—
Chromium(VI) as CrO_4^-	3	100	—
Cobalt	10	1 000	—
Copper (soluble)	10	300	—
Cyanide free	1	30	—
Formaldehyde	10	100	—
Hydrogen peroxide	0.5	25	—
Iron(II)	3	500	—
Lead (soluble)	20	500	—
Manganese (soluble)	2	100	—
Molybdenum	5	250	—
Nitrate as NO_3^-	10	500	—
Nitrite as NO_2^-	1	80	—
Nitrite as NO_2^-	100	3 000	—
Nickel (soluble)	10	500	—
Peracetic acid	5	50	—
Phosphate (reactive)	10	500	—
Potassium	250	1 500	—
Quaternary ammonium compounds	10	1 000	as Benzalkonium chloride
Sulfate	200	1 600	—
Sulfite	10	400	—
Tin (soluble)	10	500	—
Total hardness (as $CaCO_3$)	50	375	—
Zinc	10	250	—

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BS 2690-104, *Silica: reactive, total and suspended*

BS 3145, *Specification for laboratory pH meters*

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Method 3500 Cu B Copper neocuproine method

Method 3500 Cu C Copper bathocuproine method

Method 3500 Mn, Manganese – persulfate method (oxidation to permanganate)

Method 3500 Zn B, Zinc (using) zincon

Method 4500 Br- B, Bromide phenol red colorimetric method

Method 4500 CO_2, Carbon dioxide

Method 4500 F- C, Fluoride (ion selective electrode method).

Method 4500 NO_2^- , Nitrite, colorimetric method (azo dye formation)

Method 4500 NO_3^- B, Nitrate , Ultraviolet spectrophotometric screening method

Method 4500 NO_3^- C, Nitrate, Second derivative UV spectrophotometric method

Method 4500 S^{2-} Sulfide (this gives a very good background to various sulfide methods and speciation of sulfide in waters, wastewaters and sediments)

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Standing Committee of Analysts (SCA) and Publications Catalogue:

The SCA comprises a series of working groups who provide authoritative guidance on methods of sampling and analysis for determining the quality of environmental matrices. Guidance is published as Blue Books within the series Methods for the Examination of Waters and Associated materials.

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