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Water quality — Determination of selected parameters by discrete analysis systems —

Part 2: Chromium(VI), fluoride, total alkalinity, total hardness, calcium, magnesium, iron, iron(II), manganese and aluminium with photometric detection

Qualité de l'eau — Détermination de paramètres sélectionnés par des systèmes d'analyse discrète —

Partie 2: Chrom(VI), fluorure, alcalinité totale, dureté totale, calcium, magnésium, fer, (fer(II), manganèse et aluminium avec détection photométrique

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Foreword

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

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

A list of all parts in the ISO 15923 series can be found on the ISO website.

Introduction

Many photometric determinations can be automated with a discrete analysis system. With a single instrument, a large number of different parameters can be determined, and a different combination can be specified for each sample. Working with small volumes requires less sample material and reagent.

Samples that fall outside the normal range of measurement can either be automatically diluted or analysed using a different measuring range.

Water quality — Determination of selected parameters by discrete analysis systems —

Part 2:
Chromium(VI), fluoride, total alkalinity, total hardness, calcium, magnesium, iron, iron(II), manganese and aluminium with photometric detection

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

1 Scope

This document specifies methods for the automatic determination of chromium(VI), fluoride, total alkalinity, total hardness, calcium, magnesium, iron, iron(II), manganese and aluminium with photometric determination using a discrete analysis system. The field of application is water (ground, potable, surface, waste, eluates and boiler water). The method can also be applied to marine waters with matrix matching of standard and control solutions. Note that some parameters, notably iron, manganese and aluminium and possibly chromium(VI), calcium and magnesium may not be completely quantified if the sample contains particulates. Samples can be digested in acid, as long as the buffering capacity of the reaction mixture is not exceeded. Such procedures are beyond the scope of this document, which is best suited to the determination of dissolved metals following on-site filtration.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org./obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

A discrete analysis system is an automated system for spectrophotometric and turbidimetric determinations.

The colour reactions take place in reaction cells, which may be cuvettes, in an incubator. For each determination, a separate reaction cell is used. Pre-set volumes of the sample and the reagents are pipetted into the cells and mixed.

Following the incubation period, the absorbance of the solution is measured at the wavelength applicable to the determination. Depending on which instrument is used, measurement is achieved by passing the cuvettes through the photometer or by transferring the measuring solution from the reaction cells to a photometer with a flow-through cell.

The specific chemistry for each parameter is given in the relevant annex.

5 Interferences

Particles present in the sample can lead to blockages and will interfere with the photometric measurement. Filtration of samples containing particles through a 0,45 µm membrane filter is recommended. Particles can also be removed by settlement, centrifugation or dialysis.

If the sample is filtered prior to analysis, the fraction of any of the parameters that is adsorbed onto the surface of particles will not be measured.

Inherent colour or turbidity of the sample can interfere with the analysis. Two possible procedures to correct for any inherent colour are described in Annex A.

A reliable procedure for the correction of turbidity cannot really be given. The Beer-Lambert law does not apply to turbid solutions. Furthermore, many chromogenic reagents and coloured complexes are adsorbed on particles.

Interferences specific to each parameter are discussed in the relevant annex.

6 Reagents

Reagents for each parameter are specified in Annexes B to J. Use only reagents of recognized analytical grade, unless otherwise specified in the relevant annex. Dry all solid reagents to constant weight at (105 ± 5) °C, provided that they are thermally stable. Store the dried solid in an exsiccator before weighing. Reagent volumes specified in Annexes B to J may be adjusted to suit local requirements or different instrument specifications.

For many of the reagents, calibration and control standards specified in this document, commercial preparations are available and it is quite acceptable to use them provided that manufacturer's instructions relating to storage and stability are followed.

6.1 Water, complying with the specification for grade 1 as defined in ISO 3696.

7 Apparatus

7.1 Discrete analysis system, generally consisting of the following components.

7.1.1 Sample injection device, for automated or manual operation.

7.1.2 Sample container.

7.1.3 Reagent container, refrigerated or not.

7.1.4 Incubator with temperature control, capable of maintaining a constant temperature.

7.1.5 Visible wavelength detector, e.g. spectrophotometer, suitable for a wavelength range usually between 400 nm and 880 nm.

7.1.6 Control and data processing unit.

7.1.7 Recording device, e.g. PC with software for data acquisition and evaluation.

7.2 Routine laboratory apparatus, including

7.2.1 Balance, capable of measuring to 0,000 1 g.

7.2.2 Oven.

7.2.3 Exsiccator.

7.2.4 Glassware, including volumetric flasks and beakers.

7.2.5 Autopipettes, capable of dispensing volumes from 50 µl to 500 µl.

8 Sampling and sample preparation

Use clean vessels for sampling.

Turbidity or particulates interfere with spectrophotometric detection. Using an appropriate filtration apparatus, clarify any samples containing particles by filtering through a 0,45 µm membrane (settlement, centrifugation or dialysis may also be used). To avoid contamination by the filter membrane, discard the first few millilitres of filtrate.

ISO 5667-3 offers guidance on the preparation and storage of samples. However, the stability of some of the parameters covered by this document may vary according to conditions such as the pH and other constituents present in the sample. Stability trials should be carried out locally for each matrix type. The guidance in ISO 5667-3 for preservation of samples for iron, manganese, aluminium, calcium and magnesium recommends acidifying the sample to between pH 1 and 2, but this may not be appropriate for discrete analysis methods where pH is critical, e.g. calcium and manganese. In such cases, it is important to ensure that the buffering capacity of the reaction mixture is not exceeded. Fluoride is stable for at least one month with no pre-treatment. For chromium(VI), best practice is to analyse the sample as soon as possible after sampling. ISO 18412[2] recommends a maximum of 4 d refrigerated storage, but ISO 23913[3] specifies storage for no more than 24 h at 2 °C to 5 °C.

Prepare a sample of water (6.1) in the same way as the sample, to be used as a blank.

Prepare a control standard solution from the primary control standard containing a level of analyte similar to the samples. Run it as a sample at appropriate intervals in the batch, according to local requirements. A minimum interval of once every 20 samples is recommended. Instructions for preparing a primary control standard are given in Annexes B to J.

9 Calibration

9.1 Calibration function

When the analytical system is first evaluated and at intervals afterwards, establish a calibration function for each parameter (see ISO 8466-1 or ISO 8466-2) as follows.

Using the primary calibration standard, prepare an appropriate series of calibration solutions (Annexes B to J). Use water (6.1) as a zero concentration calibration solution.

Analyse the calibration solutions according to Clause 9 and the instrument manufacturer's instructions.

Confirm the validity of the data obtained, and use to calculate the regression line as specified in ISO 8466-1 or ISO 8466-2.

During the analysis, verify the continuing validity of the established calibration function by analysing an appropriate calibration standard solution, at regular intervals according to local accuracy requirements, or at least at the end of the batch. Recalibrate, if necessary. It is recommended that calibration verification is carried out using a calibration solution in the upper third of the calibration range.

9.2 Calibration validity check

If the full calibration function is not established daily, carry out an initial calibration validity check by analysing two calibration standard solutions in the lower and upper third of the calibrated working range (see Clause 10).

Verify the continuing validity of the established calibration function as described in 9.1.

10 Procedure

Set up the discrete analysis system according to the instrument manufacturer's instructions.

Calibrate the system according to Clause 9 and the instrument manufacturer's instructions.

Prepare the samples according to Clause 8 and Annexes B to J. A consistent incubation temperature and time are essential for the stability of the absorbance measurements. Measure the absorbance of the samples using the instrument manufacturer's recommended instructions. Measure the blank according to Annex A and the instrument manufacturer's instructions.

If the absorbance of a sample exceeds that of the top calibration solution, dilute the sample using water (6.1), or reduce the sample intake by an appropriate factor to bring it into the upper half of the calibration range, and reanalyse. If necessary, subtract the absorbance of the blank from that of the samples (see Annex A).

The analytical procedure may be modified for different instruments, or to change the range or sensitivity of the method for different parameter concentrations or sample types.

11 Calculation

Calculate the mass concentration, ρ, of the parameter in question in micrograms per litre (µg/l) or milligrams per litre (mg/l) from the calibration line (see Clause 9), using the corrected absorbance values obtained (see Clause 10), as specified in ISO 8466-1 or ISO 8466-2. Take account of any dilution factors. This calculation can usually be carried out automatically using the instrument software.

12 Expression of results

Results shall be expressed as µg/l or mg/l to a maximum of three significant figures.

EXAMPLES A reading of 11,12 µg/l, rounding to: 11,1 µg/l (3 sig fig), 11 µg/l (2 sig fig), 10 µg/l (1 sig fig).

13 Test report

This test report shall contain at least the following information:

a) the test method used, together with a reference to this document, i.e. ISO/TS 15923-2:2017;

b) the details required for identification of the sample;

c) the date of the analysis;

d) the analytical results (see Clause 12);

e) any deviation from this method and a report of circumstances that may have affected the results.

Annex A
(normative)

Correction for inherent colour

A.1 General

Correction for any inherent colour in the sample is necessary. Two possible procedures are described in A.2 and A.3. Accurate correction for turbidity is not possible using these methods because the Beer-Lambert law does not apply. Discrete analysis systems can be programmed to carry out colour correction automatically.

A.2 Sample blanking

The blank absorption measurement is done after dispensing the sample and, if applicable, one or more reagents that could produce a colour change in the sample (for example because of the influence of the pH), but before dispensing the chromogenic reagent. This blank value is adjusted to take account of the ratio between the sample volumes with and without the chromogenic reagent, and subtracted from the final absorption measurement. The standards are measured in the same way.

A.3 Use of a compensating solution

When using a compensating solution, a second measuring solution is prepared using the same volumes of sample and reagent, in which the compound responsible for forming the colour is omitted. This can be achieved either by adding an equal volume of water (6.1) instead of the chromogenic reagent, or by preparing a separate reagent from which the chromogenic compound is omitted. The absorption of the compensating solution is deducted from the absorption of the sample solution.

Annex B
(normative)

Chromium(VI)

B.1 Principle

The two most common naturally occurring oxidation states of chromium are Cr(III) and Cr(VI). Cr(III) is the most stable state energetically. Cr(VI) is known to be highly toxic and mutagenic in solution, and a potent carcinogen when inhaled as a chromate dust, whereas Cr(III) has a relatively low toxicity. It is thus important to be able to routinely determine both total chromium and chromium(VI) in aqueous samples.

Chromium(VI) reacts with diphenylcarbazide in acidic solution (pH 2) to produce a red-violet colour, the absorbance of which is measured at (540 ± 10) nm.

B.2 Interferences

Vanadium produces an interference, but this is only significant at concentrations more than 10 times that of chromium. Molybdenum(VI) and mercury salts also react to form a red colour with the reagent. The red intensities are lower than those for chromium at the specified pH and concentrations of up to 200 mg/l of molybdenum and mercury can be tolerated, which are extremely unlikely to be found in the aqueous matrices covered by this document. Iron concentrations > 1 mg/l may produce a yellow colour, but this does not produce a significant interference at the specified wavelength of (540 ± 10) nm.

B.3 Reagents

B.3.1 Sulfuric acid, 95 % to 97 %.

B.3.2 Orthophosphoric acid, 1,71 g/ml.

B.3.3 1,5-Diphenylcarbazide, $C_{13}H_{14}N_4O$.

B.3.4 Ethanol, 95 %.

Alternatively, a mixture of acetone and 1-propanol dissolves possible precipitations of 1,5-diphenylcarbazide. The following solvents can be used: acetone, 1-propanol, 2-propanol, ethanol in combination with water.

B.3.5 Potassium chromate, K_2CrO_4.

B.3.6 Sodium chromate, Na_2CrO_4.

B.3.7 Acid reagent.

Carefully add 27 ml of sulfuric acid (B.3.1) and 33 ml of orthophosphoric acid (B.3.2) into 200 ml water (6.1) in a 500 ml volumetric flask and make up to the mark with water.

This solution is stable for at least 12 months at room temperature.

B.3.8 Chromogenic reagent.

Dissolve 0,50 g 1,5-diphenylcarbazide (B.3.3) in 100 ml ethanol (B.3.4) and make up to 500 ml with acid reagent (B.3.7). Mix and store in an amber bottle.

This solution is stable for three weeks when stored at 2 °C to 8 °C.

B.3.9 Primary calibration standard, chromium(VI), ρ(Cr) = 100 mg/l.

Dissolve 0,373 5 g potassium chromate (B.3.5) in a 1 000 ml volumetric flask containing approximately 750 ml of water (6.1). Make up to the mark with water.

This solution is stable for at least one month at room temperature.

B.3.10 Primary control standard, chromium(VI), ρ(Cr) = 50 mg/l.

Dissolve 0,155 8 g sodium chromate (B.3.6) in a 1 000 ml volumetric flask containing approximately 750 ml of water (6.1). Make up to the mark with water.

This solution is stable for at least one week at room temperature.

B.3.11 Working calibration solutions, e.g. working range 0,05 mg/l to 0,5 mg/l Cr.

Into a series of 100 ml volumetric flasks, pipette 50 µl, 100 µl, 200 µl, 300 µl, 400 µl and 500 µl of primary calibration standard (B.3.9) and make up to the mark with water (6.1), to give calibration solutions containing 0,05 mg/l, 0,1 mg/l, 0,2 mg/l, 0,3 mg/l, 0,4 mg/l and 0,5 mg/l Cr.

Prepare freshly on the day of use.

B.3.12 Control solution.

Pipette a specific volume of primary control standard (B.3.10) into a volumetric flask and make up to the mark with water (6.1). Select a volume to give a final concentration of Cr(VI) in the same range as real samples.

B.4 Procedure

B.4.1 Calibration

The calibration curve is polynomial/second order.

B.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— 9 parts of sample;

— 1 part of chromogenic reagent (B.3.8).

Mix the solution after each addition.

The recommended maximum incubation time is 600 s. A lower incubation time may be used if the incubation temperature is in the upper half of the quoted range.

Measure the absorbance at (540 ± 10) nm.

NOTE A typical calibration range for the method is 0,05 mg/l to 0,5 mg/l Cr.

Annex C
(normative)

Fluoride

C.1 Principle

Fluoride reacts with Ce^{3+} and alizarin-3-methyliminodiacetic acid in acidic solution to produce a violet colour, the absorbance of which is measured at (630 ± 10) nm.

C.2 Interferences

Chlorine interferes. It can be removed by heating the water sample or stripping with nitrogen. Phosphate concentrations above 1 mg/l P interfere and high levels of other phosphorus containing anions may also interfere. Aluminium forms an extremely stable fluoro compound, AlF_6^{-3}. This is overcome by treatment with 8-hydroxyquinoline to complex the aluminium and by subsequent extraction with chloroform. At aluminium levels below 0,2 mg/l, the extraction procedure is not required. Fluoride forms stable complexes with other high valency cations, but these are not normally found in typical water samples. To obtain the total concentration of fluoride in samples containing a high concentration of dissolved or suspended solids, or organic matter, a preliminary acid distillation step is necessary, but the procedure is beyond the scope of this document.

C.3 Reagents

C.3.1 Ammonia solution, 25 %.

C.3.2 Alizarin-3-methyliminodiacetic acid, $C_{19}H_{15}NO_8$.

C.3.3 Acetic acid, glacial.

C.3.4 Sodium acetate trihydrate, $C_2H_9NaO_5$.

C.3.5 Cerium nitrate, $Ce(NO_3)_3$.

C.3.6 Sodium fluoride, NaF.

C.3.7 Potassium fluoride, KF.

C.3.8 Nitric acid, 65 %.

C.3.9 Chromogenic reagent.

Suspend (0,192 ± 0,1) g alizarin-3-methyliminodiacetic acid (C.3.2) in 50 ml water (6.1) and dissolve by adding 0,5 ml ammonia (C.3.1). Dilute the mixture with approximately 350 ml water (6.1)) and adjust the pH to between 4,0 and 5,0 by adding acetic acid (C.3.3). Pour this solution into a 500 ml volumetric flask and make up to the mark with water (6.1). Store in an amber bottle.

This solution is stable for one month at room temperature.

C.3.10 Acetate buffer solution.

Dissolve (30,0 ± 0,1) g sodium acetate-trihydrate (C.3.4) in approximately 300 ml water in a 500 ml volumetric flask, add 57,5 ml acetic acid (C.3.3) and make up to the mark with water (6.1).

The solution is stable for six months at room temperature.

C.3.11 Cerium nitrate solution.

Dissolve (0,217 ± 0,1) g cerium nitrate (C.3.5) in approximately 400 ml water (6.1) in a 500 ml volumetric flask, add 0,1 ml nitric acid (C.3.8) and make up to the mark with water (6.1).

This solution is stable for one month at room temperature.

C.3.12 Primary calibration standard fluoride, ρ(F) = 100 mg/l.

Dissolve (0,221 ± 0,001) g sodium fluoride (C.3.6) in a 1 000 ml volumetric flask in approximately 750 ml of water (6.1). Make up to the mark with water (6.1).

This solution is stable for three months at room temperature.

C.3.13 Primary control standard fluoride, ρ(F) = 100 mg/l.

Prepare the control standard solution using a different starting material to that for the primary calibration standard, for example:

Dissolve (0,306 ± 0,001) g potassium fluoride (C.3.7) in a 1 000 ml volumetric flask in approximately 750 ml of water (6.1). Make up to the mark with water (6.1).

The solution is stable for three months at room temperature.

C.3.14 Working calibration solutions, e.g. working range 0,2 mg/l to 2,0 mg/l F.

Into a series of 100 ml volumetric flasks, pipette 200 µl, 400 µl, 800 µl, 1 200 µl, 1 600 µl and 2 000 µl of primary calibration standard (C.3.12) and make up to the mark with water (6.1), to give calibration solutions containing 0,20 mg/l, 0,40 mg/l, 0,80 mg/l, 1,2 mg/l, 1,6 mg/l and 2,0 mg/l F.

C.3.15 Control solution.

Pipette a specific volume of primary control standard (C.3.13) into a volumetric flask and make up to the mark with water (6.1). Select a volume to give a final concentration of fluoride in the same range as real samples.

C.4 Procedure

C.4.1 Calibration

The calibration curve is usually of first order.

C.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— 26 parts of sample;

— 7 parts water (6.1);

— 12 parts of chromogenic reagent (C.3.9) and 18 parts of water (6.1).

Mix the solution after each addition.

Incubate for a recommended time of 120 s.

— Add 2,2 parts of actetate buffer solution (C.3.10) and 7 parts of water (6.1).

Incubate for a recommended time of 240 s.

— Add 9 parts of cerium nitrate (C.3.11) and 18 parts of water (6.1).

Incubate for a recommended time of 600 s.

Measure the absorbance at (630 ± 10) nm.

NOTE A typical calibration range for the method is 0,2 mg/l to 2 mg/l F.

Annex D
(normative)

Total alkalinity

D.1 Principle

The sample is reacted with weak buffer and methyl orange indicator. The pH shift caused by the sample affects the methyl orange colour. The colour changes from red at pH 3 to yellow at pH 4,5. The decrease in colour of the indicator is measured spectrophotometrically at (550 ± 10) nm and is proportional to the alkalinity of the sample.

D.2 Interferences

Oxidizing agents may bleach the methyl orange indicator causing falsely high results, but it is unlikely that they will be found in typical water samples.

D.3 Reagents

D.3.1 Hydrochloric acid, 1 mol/l.

D.3.2 Methyl orange, $C_{14}H_{14}N_3NaO_3S$.

D.3.3 Potassium hydrogen phthalate, $C_8H_5KO_4$.

D.3.4 Sodium carbonate, anhydrous, Na_2CO_3.

D.3.5 Methyl orange stock solution.

Dissolve 0,062 5 g of methyl orange in approximately 300 ml water (6.1) in a 500 ml volumetric flask. Make up to the mark with water (6.1).

This solution is stable for one month at room temperature.

D.3.6 Buffer solution, pH 3,1.

Dissolve 2,552 g potassium hydrogen phthalate (D.3.3) in approximately 300 ml water (6.1) in a 500 ml volumetric flask. Add 4,38 ml of hydrochloric acid (D.3.1) and make upto the mark with water (6.1). Check that the pH is 3,1 ± 0,1 and correct if necessary.

This solution is stable for one month at room temperature.

D.3.7 Working methyl orange/buffer solution.

Add 15 ml of pH 3,1 buffer solution (D.3.6) to 3 ml of methyl orange stock solution (D.3.5) and mix thoroughly.

This solution is stable for one month at room temperature.

D.3.8 Primary calibration standard alkalinity, 1 ml = 1,00 mg $CaCO_3$.

Weigh 1,059 g of anhydrous sodium carbonate (D.3.4) into a 1 000 ml volumetric flask. Dissolve in approximately 500 ml of water (6.1). Make up to the mark with water (6.1).

This solution is stable for at least one month at room temperature.

D.3.9 Primary control standard, alkalinity, 1 ml = 1,00 mg $CaCO_3$.

Prepare using a different starting material to that used for the primary calibration standard.

This solution is stable for at least one month at room temperature.

D.3.10 Working calibration solutions, e.g. working range 10 mg/l to 200 mg/l $CaCO_3$.

Into a series of 100 ml volumetric flasks, pipette 1,0 ml, 2,0 ml, 4,0 ml, 6,0 ml, 8,0 ml, 10,0 ml, 15,0 ml and 20,0 ml of primary calibration standard (D.3.8) and make up to the mark with water (6.1), to give calibration solutions containing alkalinity equivalent to 10 mg/l, 20 mg/l, 40 mg/l, 60 mg/l, 80 mg/l, 100 mg/l, 150 mg/l and 200 mg/l $CaCO_3$.

D.3.11 Control solution.

Pipette a specific volume of primary control standard (D.3.9) into a volumetric flask and make up to the mark with water (6.1). Select a volume to give a final concentration of alkalinity in the same range as real samples.

D.4 Procedure

D.4.1 Calibration

The calibration curve is usually first order.

D.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— 1,6 parts of sample;

— 1 part of working methyl orange/buffer solution (D.3.7).

Mix the solution after each addition.

The recommended incubation time is 600 s.

Measure the absorbance at (550 ± 10) nm.

NOTE A typical calibration range for the method is 10 mg/l to 200 mg/l as $CaCO_3$.

Annex E
(normative)

Total hardness

E.1 Principle

Total hardness is typically the sum of magnesium and calcium in water. Strontium and barium also contribute, but they are usually present at insignificant concentrations relative to calcium and magnesium.

Magnesium forms a complex with ethylenediaminetetraacetic acid (EDTA), which is less stable than the complex formed by calcium or other cations. Thus, calcium in the sample displaces magnesium from the Mg-EDTA complex. The free magnesium ions in the solution (originally present and displaced) react with calmagite at a pH of 10 to form a red/violet complex. The absorbance of this complex at (520 ± 10) nm is measured and provides an accurate assessment of total hardness.

E.2 Interference

Metal cations other than calcium, that form strong EDTA complexes, may also displace magnesium, causing a high result, but they are usually present at very low concentration relative to calcium and can be ignored.

E.3 Reagents

E.3.1 **EDTA**, magnesium disodium salt, $C_{10}H_{12}MgN_2Na_2O_8$.

E.3.2 **Sodium tetraborate decahydrate**, $Na_2B_4O_7{\cdot}10H_2O$.

E.3.3 **Sodium hydroxide**, NaOH.

E.3.4 **Calmagite**, $C_7H_{14}N_2O_5S$.

E.3.5 **Calcium carbonate**, $CaCO_3$.

E.3.6 **Hydrochloric acid**, 1 mol/l.

E.3.7 **EDTA**, magnesium disodium solution, 0,2 g/l.

Dissolve 0,2 g of EDTA, magnesium disodium salt (E.3.1) in approximately 500 ml of water (6.1) in a 1 000 ml volumetric flask. Make up to the mark with water (6.1).

This solution is stable for at least one month stored at 2 °C to 8 °C.

E.3.8 **Sodium tetraborate solution**, 0,025 mol/l.

Dissolve 9,53 g of sodium tetraborate decahydrate (E.3.2) in approximately 500 ml of water (6.1) in a 1 000 ml volumetric flask. Make up to the mark with water (6.1).

This solution is stable for at least one month at room temperature.

E.3.9 Sodium hydroxide solution, 0,1 mol/l.

Dissolve 4,0 g of sodium hydroxide (E.3.3) in approximately 500 ml of water (6.1) in a 1 000 ml volumetric flask. Make up to the mark with water (6.1).

This solution is stable for at least one month at room temperature.

E.3.10 pH 10 buffer solution.

Add 50 ml of sodium tetraborate solution (E.3.8) to a 100 ml volumetric flask. Add 18,3 ml of sodium hydroxide solution (E.3.9) to the flask and make up to the mark with water (6.1).

This solution is stable for at least one month at room temperature.

E.3.11 Calmagite indicator solution.

Dissolve 0,25 g calmagite (E.3.4) in 500 ml of water (6.1) by stirring approximately 30 min on a magnetic stirrer. Filter through a 0,45 µm filter membrane before use.

This solution is stable for at least one month at room temperature.

E.3.12 Primary calibration standard hardness, 1 ml = 1,00 mg $CaCO_3$.

Add 0,100 g of calcium carbonate (E.3.5) to approximately 80 ml of water (6.1) in a 100 ml volumetric flask. Gradually add hydrochloric acid (E.3.6) (approx. 2 ml) to dissolve the calcium carbonate. Make up to the mark with water (6.1).

This solution is stable for at least one month at room temperature.

E.3.13 Primary control standard hardness, 1 ml = 1,00 mg $CaCO_3$.

Prepare using a different starting material to that used for the primary calibration standard.

This solution is stable for at least one month at room temperature.

E.3.14 Working calibration solutions, e.g. working range 10 mg/l to 200 mg/l $CaCO_3$.

Into a series of 100 ml volumetric flasks, pipette 1,0 ml, 2,0 ml, 4,0 ml, 6,0 ml, 8,0 ml, 10,0 ml, 15,0 ml and 20,0 ml of primary calibration standard (E.3.12) and make up to the mark with water (6.1), to give calibration solutions containing hardness equivalent to 10 mg/l, 20 mg/l, 40 mg/l, 60 mg/l, 80 mg/l, 100 mg/l, 150 mg/l and 200 mg/l $CaCO_3$.

E.3.15 Control solution.

Pipette a specific volume of primary control standard (E.3.13) into a volumetric flask and make up to the mark with water (6.1). Select a volume to give a final concentration of hardness in the same range as real samples.

E.4 Procedure

E.4.1 Calibration

The calibration curve is nonlinear, second order.

E.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— 1 part of sample;

— 44 parts of water (6.1);

— 22 parts of EDTA, magnesium disodium solution (E.3.7);

— 22 parts of pH 10 buffer solution (E.3.10);

— 4 parts of calmagite indicator solution (E.3.11).

Mix the solution after each addition.

Incubate for a recommended time of 600 s.

Measure the absorbance at (520 ± 10) nm.

NOTE A typical calibration range for the method is 10 mg/l to 200 mg/l as $CaCO_3$.

Annex F
(normative)

Calcium

F.1 Principle

Calcium ions form a highly coloured complex with arsenazo(III) at neutral pH.

The absorbance due to the resulting complex is measured at (660 ± 10) nm.

F.2 Interference

There are no identified interferences in the analytical range of interest.

F.3 Reagents

F.3.1 Arsenazo(III), $C_{22}H_{18}As_2N_4O_{14}S_2$.

F.3.2 Imidazole, $C_3H_4N_2$.

F.3.3 Sodium dodecyl sulfate solution, $NaC_{12}H_{25}SO_4$, 10 %.

F.3.4 Calcium carbonate, $CaCO_3$.

F.3.5 Hydrochloric acid, 1 mol/l.

F.3.6 Chromogenic reagent, arsenazo(III), ρ = 0,2 mmol/l, imidazole, ρ = 100 mmol/l.

Dissolve 6,81 g imidazole (F.3.2) in approximately 700 ml of water (6.1) in a volumetric flask. Add 0,155 g arsenazo(III) (F.3.1) and shake to dissolve. Add 1 ml of sodium dodecyl sulfate solution (F.3.3) and make up to the mark with water (6.1).

This reagent is stable for at least one week if stored at 2 °C to 8 °C.

F.3.7 Primary calibration standard, 1 ml = 1,00 mg Ca.

Add 0,250 g of calcium carbonate (F.3.4) to approximately 80 ml of water (6.1) in a 100 ml volumetric flask. Gradually add 1 M hydrochloric acid (F.3.5) (approx. 5 ml) to dissolve the calcium carbonate. Make up to the mark with water (6.1).

This solution is stable for at least one month at room temperature.

F.3.8 Primary control standard hardness, 1 ml = 1,00 mg Ca.

Prepare using a different starting material to that used for the primary calibration standard.

This solution is stable for at least one month at room temperature.

F.3.9 Working calibration solutions, e.g. working range 10 mg/l to 200 mg/l Ca.

Into a series of 100 ml volumetric flasks, pipette 1,0 ml, 2,0 ml, 4,0 ml, 6,0 ml, 8,0 ml, 10,0 ml, 15,0 ml and 20,0 ml of primary calibration standard (F.3.7) and make up to the mark with water (6.1), to give calibration solutions containing calcium at 10 mg/l, 20 mg/l, 40 mg/l, 60 mg/l, 80 mg/l, 100 mg/l, 150 mg/l and 200 mg/l Ca.

F.3.10 Control solution.

Pipette a specific volume of primary control standard (F.3.8) into a volumetric flask and make up to the mark with water (6.1). Select a volume to give a final concentration of calcium in the same range as real samples.

F.4 Procedure

F.4.1 Calibration

The calibration curve is nonlinear/second order.

F.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— 50 parts of chromogenic reagent (F.3.6);

— 7 parts of water (6.1).

Mix the solution after each addition.

Incubate for a recommended time of 180 s.

— Add 1 part of sample and 5 parts of water (6.1).

Incubate for a recommended time of 180 s.

Measure the absorbance at (660 ± 10) nm.

NOTE A typical calibration range for the method is 10 mg/l to 200 mg/l Ca.

Annex G
(normative)

Magnesium

G.1 Principle

Xylidyl blue forms a red coloured complex with magnesium in alkaline conditions.

The absorbance due to the resulting complex is measured at (520 ± 10) nm.

G.2 Interference

A potential interference from calcium is removed by use of ethylene glycol tetraacetic acid (EGTA). There are no other known interferences in the range of interest. For high levels of calcium, it may be necessary to add additional EGTA reagent. Samples should be tested to assess the level of interference.

G.3 Reagents

G.3.1 Xylidyl blue, sodium salt, $C_{25}H_{20}N_3NaO_6S$.

G.3.2 Trisaminomethane (Tris), $C_4H_{11}NO_3$.

G.3.3 Ethylene glycol tetraacetic acid (EGTA), $C_{14}H_{24}N_2O_{10}$.

G.3.4 Potassium carbonate, K_2CO_3.

G.3.5 Sodium hydroxide, 1 mol/l.

G.3.6 Magnesium carbonate, $MgCO_3$.

G.3.7 Hydrochloric acid, 1 mol/l.

G.3.8 EGTA solution, 50 mmol/l.

Add 0,19 g EGTA (G.3.3) to a 10 ml volumetric flask. Pipette 1,7 ml of sodium hydroxide (G.3.5) into the flask and make up to the mark with water (6.1).

This solution is stable for at least one month at room temperature.

G.3.9 Chromogenic reagent.

Dissolve 2,42 g Tris (G.3.2) and 1,06 g of potassium carbonate (G.3.4) in approximately 50 ml of water (6.1) in a 100 ml volumetric flask. Pipette 1 ml of EGTA solution, 50 mmol/l (G.3.8) into the flask and shake to mix the contents. Add 0,072 g of xylidyl blue, sodium salt (G.3.1) and shake to dissolve. Make up to the mark with water (6.1).

This reagent is stable for at least one week if stored at 2 °C to 8 °C.

G.3.10 Primary calibration standard, 1 ml = 1,00 mg Mg.

Add 0,347 g of magnesium carbonate (G.3.6) to approximately 80 ml of water in a 100 ml volumetric flask. Gradually add hydrochloric acid (G.3.7) (approx. 5 ml) to dissolve the magnesium carbonate. Make up to the mark with water (6.1).

This solution is stable for at least one month at room temperature.

G.3.11 Primary control standard magnesium, 1 ml = 1,00 mg Mg.

Prepare using a different starting material to that used for the primary calibration standard.

This solution is stable for at least one month at room temperature.

G.3.12 Working calibration solutions, e.g. working range 5 mg/l to 70 mg/l Mg.

Into a series of 100 ml volumetric flasks, pipette 0,5 ml, 1,0 ml, 2,0 ml, 3,0 ml, 4,0 ml, 5,0 ml, 6,0 ml and 7,0 ml of primary calibration standard (G.3.10) and make up to the mark with water (6.1), to give calibration solutions containing magnesium at 5 mg/l, 10 mg/l, 20 mg/l, 30 mg/l, 40 mg/l, 50 mg/l, 60 mg/l and 70 mg/l Mg.

G.3.13 Control solution.

Pipette a specific volume of primary control standard (G.3.11) into a volumetric flask and make up to the mark with water (6.1). Select a volume to give a final concentration of magnesium in the same range as real samples.

G.4 Procedure

G.4.1 Calibration

The calibration curve is usually second order.

G.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— 100 parts of chromogenic reagent (G.3.9);

— 10 parts of water (6.1).

Mix the solution after each addition.

Incubate for a recommended time of 180 s.

— Add 1 part of sample and 12 parts of water (6.1).

Incubate for a recommended time of 180 s.

Measure the absorbance at (520 ± 10) nm.

NOTE A typical calibration range for the method is 5 mg/l to 70 mg/l mg.

Annex H
(normative)

Iron(II) and iron (total)

H.1 Principle

Iron(II) reacts with 1,10-phenanthroline to form an orange-red coloured dye which is stable at pH 2,5 to 9. If the sample is filtered before analysis (Clause 8), only dissolved iron is determined, which is mainly iron(II). Iron(III) compounds are generally quite insoluble. If the sample is treated with acid prior to filtration, total iron can be determined. Depending on the sample type, a more or less vigorous acid treatment may be needed to dissolve all of the iron. Care is needed to ensure that the buffer can maintain the pH in the correct range. A detailed description of different acid treatments is beyond the scope of this document.

To determine the sum of iron(II) and iron(III) a reduction step is added before the chromogenic reaction, using hydroxylamine hydrochloride at a pH between 3,4 and 5,5.

The absorbance is measured at (500 ± 20) nm.

H.2 Interferences

Interferences by copper, cobalt and zinc occur at concentrations 10 times higher than that of iron. The presence of excess 1, 10-phenanthroline helps to minimize such cationic interferences.

H.3 Reagents

H.3.1 Ammonium acetate, $C_2H_7NO_2$.

Sodium acetate may be used as an alternate.

H.3.2 Acetic acid, glacial.

H.3.3 1,10-phenanthroline, $C_{12}H_8N_2$.

H.3.4 Hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$.

H.3.5 Ammonium iron(II) sulfate hexahydrate, $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$.

H.3.6 Sulfuric acid, > 95 %.

H.3.7 Hydrochloric acid, 35 % to 37 % may be used as an alternate.

H.3.8 Ammonium acetate-acetic acid buffer.

In a 100 ml volumetric flask, dissolve (40,0 ± 0,1) g ammonium acetate (H.3.1) and 50 ml acetic acid (H.3.2) and make up to 100 ml with water (6.1).

The solution is stable for three months at room temperature.

NOTE Alternatively, (40 ± 0,1) g sodium acetate can be used in place of ammonium acetate.

H.3.9 Chromogenic reagent.

In a 100 ml volumetric flask, dissolve (0,50 ± 0,01) g 1,10-phenanthroline (H.3.3) in water (6.1) and make up to 100 ml with water (6.1).

The solution is stable for three weeks if stored in the dark at 2 °C to 8 °C.

H.3.10 Hydroxylamine hydrochloride, ρ = 100 g/l.

In a 100 ml volumetric flask, dissolve (10,0 ± 0,1) g hydroxylamine hydrochloride (H.3.4) in water (6.1) and make up to 100 ml with water (6.1).

The solution is stable for three weeks at 2 °C to 8 °C.

H.3.11 Primary calibration standard iron, ρ(Fe) = 100 mg/l.

Weigh (0,702 ± 0,001) g ammonium iron(II) sulfate hexahydrate (H.3.6) into a 1 000 ml flask. Add approximately 200 ml water (6.1) followed by 4 ml sulfuric acid (alternatively 15 ml hydrochloric acid (H.3.7)), and stir to dissolve. Dilute to the mark with water (6.1).

The solution is stable for one month if stored dark at 2 °C to 8 °C.

H.3.12 Primary control standards, iron(II) and iron(III), ρ(Fe) = 100 mg/l.

Prepare the iron(II) control standard using a different source material from that used to prepare the primary calibration standard, or in the case of a commercially sourced standard, use a different supplier. An additional commercially sourced iron(III) control standard may be used as a check on the reduction step.

H.3.13 Working calibration solutions, e.g. working range 0,05 mg/l to 1,0 mg/l Fe.

Into a series of 100 ml volumetric flasks, pipette 50 µl, 100 µl, 200 µl, 400 µl, 600 µl, 800 µl and 1 000 µl of primary calibration standard (H.3.11) and make up to the mark with water (6.1), to give calibration solutions containing: 0,05 mg/l, 0,1 mg/l, 0,2 mg/l, 0,4 mg/l, 0,6 mg/l, 0,8 mg/l and 1,0 mg/l Fe.

Prepare freshly on the day of use.

H.3.14 Control solutions, iron(II) and iron(III).

Pipette a specific volume of primary control standard (H.3.12) into a volumetric flask and make up to the mark with water (6.1). Select a volume to give a final concentration of Fe in the same range as real samples. An additional iron(III) control solution (H.3.12) may also be prepared as a check on the reduction step.

H.4 Procedure

H.4.1 Calibration

The calibration curve is usually first order.

H.4.2 Analysis

The incubation temperature lies between 20 °C and 40 °C. Prepare a measuring solution typically made up of the following:

— a maximum of 20 parts of a sample by volume;

— 2 parts of ammonium acetate-acetic acid buffer (H.3.8);

— 1 part of hydroxylamine hydrochloride, ρ = 100 g/l (H.3.10) – **omit if only Fe(II) is being determined.**

Mix the measuring solution after each addition.

Incubate for a recommended time of 60 s.

— Add 1 part of chromogenic reagent (H.3.9).

Incubate for a recommended time of 900 s.

Measure the absorbance at (500 ± 20) nm.

NOTE A typical calibration range for the method is 0,05 mg/l to 1,0 mg/l Fe.

Annex I
(normative)

Manganese

I.1 Principle

Manganese as Mn(II) reacts with formaldoxime at a pH between 9,5 and 10,5 to produce a compound with an orange-red colour. Manganese(II) compounds are soluble, other forms of manganese may be present as insoluble matter. Pre-treatment may be necessary to convert other forms of manganese to Mn(II) if determination of total manganese is required, but see I.2 below.

The absorbance is measured at (460 ± 10) nm.

I.2 Interferences

Interference by Fe^{2+} ions is masked by ethylenediaminetetraacetic acid (EDTA) and hydroxlamine hydrochloride. Uranium, molybdenum and chromium will form complexes with formaldoxime, but of a very light colour and so do not interfere. The magnitude of any possible interferences should be assessed beforehand.

If the samples are treated with a strong acid prior to analysis, the buffering capacity of the reaction mixture may be exceeded and the pH may fall below the required range for colour development.

I.3 Reagents

I.3.1 **Sodium hydroxide**, NaOH.

I.3.2 **Ammonium hydroxide**, NH_4OH, ρ = 0,91 g/ml.

I.3.3 **Hydroxylamine hydrochloride**, $NH_2OH.HCl$.

I.3.4 **Formaldehyde solution**, H_2CO, 35 %.

I.3.5 **Ethylenediaminetetraacetic acid**, tetrasodium salt (EDTA), $C_{10}H_{12}N_2Na_4O_8$.

I.3.6 **Manganese sulfate monohydrate**, $MnSO_4 \cdot H_2O$

I.3.7 **Hydrochloric acid**, 35 % to 37 %, 11,7 mol/l.

I.3.8 **Sodium hydroxide stock solution**, ρ = 160 g/l.

In a 100 ml volumetric flask, dissolve (16,0 ± 0,1) g sodium hydroxide (I.3.1) in water (6.1) and make up to the mark with water (6.1).

The solution is stable for one month at room temperature.