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Water quality — Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection

The European Standard EN ISO 15682:2001 has the status of a British Standard

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National foreword

This British Standard is the official English language version of EN ISO 15682:2001(as corrected). It is identical with ISO 15682:2000.

The UK participation in its preparation was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, chemical and biochemical methods, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled “International Standards Correspondence Index”, or by using the “Find” facility of the BSI Standards Electronic Catalogue.

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Summary of pages

This document comprises a front cover, an inside front cover, the EN ISO title page, the EN ISO foreword page, the ISO title page, pages ii to v, a blank page, pages 1 to 21, the annex ZA page, and inside back cover and a back cover.

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EUROPEAN STANDARD
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EN ISO 15682

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English version

Water quality - Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection (ISO 15682:2000)

Qualité de l'eau - Dosage du chlorure par analyse en flux (CFA et FIA) et par détection photométrique ou potentiométrique (ISO 15682:2000)

Wasserbeschaffenheit - Bestimmung von Chlorid mittels Fließanalyse (CFA und FIA) und photometrischer oder potentiometrischer Detektion (ISO 15682:2000)

This European Standard was approved by CEN on 18 June 2001.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Foreword

The text of the International Standard from Technical Committee ISO/TC 147, 'Water quality' of the International Organization for Standardization (ISO) has been taken over as an European Standard by Technical Committee CEN/TC 230,'Water analysis', the Secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2002, and conflicting national standards shall be withdrawn at the latest by February 2002.

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

NOTE: Normative references to International Standards are listed in annex ZA (normative).

INTERNATIONAL STANDARD

ISO 15682

First edition
2000-07-15

Water quality — Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection

Qualité de l'eau — Dosage du chlorure par analyse en flux (CFA et FIA) et par détection photométrique ou potentiométrique

Reference number
ISO 15682:2000(E)

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15682 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annexes A, B and C of this International Standard are for information only.

Introduction

Methods using flow analysis automatize wet chemical procedures and are particularly suitable for the processing of many analytes in water in large sample series at a high analysis frequency (up to 100 samples per hour).

Differentiation is required between flow injection analysis (FIA) [1, 2], and continuous flow analysis (CFA) [3]. Both methods share the feature of automatic dosage of the sample into a flow system (manifold) where the analytes in the sample react with the reagent solutions on their way through the manifold. The sample preparation may be integrated in the manifold. The amount of reaction product is measured in a flow detector (e.g. photometer, or ion-selective electrode). The detector produces a signal from which the concentration of the parameter is calculated.

It should be investigated whether and to what extent particular problems will require the specification of additional marginal conditions.

Water quality — Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection

1 Scope

This International Standard specifies two methods for the determination of chloride by flow analysis. The two basic methods are covered in separate clauses as follows:

a) Clause 3: Determination of chloride by flow analysis and photometric detection.

b) Clause 4: Determination of chloride by flow analysis and potentiometric detection.

Both methods are applicable to the analysis of water and waste water (including leachates) containing chloride in the concentration range from 1 mg/l to 1 000 mg/l. On a case-by-case basis the range of the analysis can be changed.

After dilution, samples with a chloride concentration > 1 000 mg/l can also be analysed.

The method with potentiometric detection is also applicable to turbid and/or coloured samples.

NOTE From the ecological point of view, the potentiometric method is preferable because it avoids the use of toxic reagents. When the photometric method is applied, volatile and solid wastes containing mercury should be discarded in accordance with environmental regulations.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, this publication do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

3 Determination of chloride by flow analysis (FIA and CFA) with photometric detection

3.1 Principle

When using FIA, the sample is injected into a continuous flowing carrier stream (water) through an injection valve. When using CFA, the sample is pumped into the carrier stream via a peristaltic pump. Depending on the concentration of the sample, the sample is diluted with water. A reagent solution (mercury thiocyanate iron(III) nitrate solution), also pumped by the peristaltic pump, is then mixed with the sample stream. The thiocyanate, which is liberated by the chloride, reacts with the iron(III) ions to form a red-coloured iron(III) thiocyanate complex [4], [5], [6].

It is absolutely essential that the tests described in this International Standard be carried out by suitably qualified staff.

3.2 Interferences

The analysis is subject to interferences as follows:

a) chemicals which liberate thiocyanate (i.e. the mercury thiocyanate), for example bromide and iodide ions;

Bromide causes interference when present in concentrations exceeding 30 mg/l. The mass concentration of bromide and iodide can be determined in terms of chloride equivalents, and the result can be considered in the calculation procedure (3.7).

b) chemicals which form a coloured product with the reagent used in the analysis (e.g. thiocyanate and sulfide ions);

When sulfide ions are expected (in surface, waste and drain waters), the sample should be treated with 0,5 ml of hydrogen peroxide (3.3.7) per 100 ml of sample and analysed after at least 5 min.

c) the natural colour of the sample.

In this case dilution of the sample or in-line dialysis is recommended.

Filtration of the sample before analysis is advisable for samples with particle sizes larger than 100 µm (for example surface and waste waters), otherwise the particles in the sample may clog the transport tubes.

The pH of the sample shall be adjusted to a value between pH 3 and pH 10.

The self-absorbance of the sample matrix can be compensated for by measuring, in addition to the sample signal (3.6.5), the signal of the sample in a parallel channel without the admixture of the reagents. The parallel channel can be integrated into the flow system (3.4.1 or 3.4.2). In this case the difference between the two responses (with and without addition of reagents) is used for the calculation of results (in accordance with 3.7). The difference between the two measured signals is used in equation (2) (3.7).

3.3 Reagents

All chemicals required shall be of recognized analytical grade.

3.3.1 **Water**, of grade 1, in accordance with ISO 3696.

3.3.2 **Mercury(II) thiocyanate,** $Hg(SCN)_2$.

WARNING — Volatile and solid wastes containing mercury should be discarded in accordance with environmental regulations.

3.3.3 **Methanol**, CH_3OH.

WARNING — Methanol is toxic and should be handled with care.

3.3.4 **Nitric acid I**, HNO_3, $\rho = 1{,}4$ g/ml, mass fraction = 65 %.

3.3.5 **Iron(III) nitrate nonahydrate,** $Fe(NO_3)_3 \cdot 9H_2O$.

3.3.6 **Sodium chloride**, NaCl, dried at 105 °C ± 5 °C.

3.3.7 **Hydrogen peroxide**, H_2O_2, $\rho = 1{,}11$ g/ml, mass fraction = 30 %.

3.3.8 **Detergent solution**, polyethyleneglycol dodecyl ether, $HO\text{-}CH_2CH_2\text{-}O\text{-}C_{12}H_{25}$.

Freezing range 33 °C to 41 °C, solution, mass fraction = 30 %.

The solution is stable for one month.

3.3.9 Reagent solution (R in Figures B.1 to B.4).

a) Dissolve 31 g of iron(III) nitrate nonahydrate (3.3.5) in approximately 500 ml of water.

b) In a 1 000 ml volumetric flask dissolve 0,62 g of mercury thiocyanate (3.3.2) in 150 ml of methanol (3.3.3) while constantly stirring. Add 100 ml of water (3.3.1), 3,4 ml of nitric acid I (3.3.4), and the above-mentioned aqueous solution of iron nitrate. Make up to volume with water (3.3.1). Stir the solution for 2 h and filter.

   The solution is stable for three months in a dark place.

c) Before analysis, degas the reagents for 10 min, e.g. by membrane filtration (under pressure).

3.3.10 Chloride stock solution I, ρ = 10 000 mg/l.

Dissolve 16,50 g ± 0,05 g of sodium chloride (3.3.6) in water (3.3.1) and make up to a volume of 1 000 ml with water.

The solution is stable for one year.

3.3.11 Chloride stock solution II, ρ = 100 mg/l.

Add 5 ml of stock solution I (3.3.10) in a 500 ml volumetric flask and make up to volume with water.

The solution is stable for three months.

3.3.12 Carrier solution for FIA (C1 in Figures B.1 and B.2).

Water (3.3.1) shall be used.

3.3.13 Carrier solutions for CFA (C2 and C3 in Figure B.4).

- **C2**: Dilute 8 ml of nitric acid I (3.3.4) in approximately 900 ml of water in a 1 000 ml volumetric flask. Add 1 ml of detergent solution (3.3.8) and make up to volume with water.
- **C3**: Dilute 4 ml of nitric acid I (3.3.4) in approximately 900 ml of water in a 1 000 ml volumetric flask. Add 1 ml of detergent solution (3.3.8) and make up to volume with water.

3.3.14 Calibration solutions.

Prepare the calibration solutions by diluting stock solution I or II (3.3.10 or 3.3.11).

Use a minimum of at least five calibration standards per working range. For example, if six standards are used, proceed for the working ranges I to III as follows:

a) Range III (1 mg/l to 10 mg/l):

   Pipette 1 ml, 3 ml, 5 ml, 6 ml, 8 ml, and 10 ml respectively of stock solution II (3.3.11) into a series of 100 ml volumetric flasks. Make up to volume with water.

   The mass concentrations of chloride in the resulting calibration solution are 1 mg/l, 3 mg/l, 5 mg/l, 6 mg/l, 8 mg/l, and 10 mg/l respectively. These calibration solutions are stable for one week.

b) Range II (10 mg/l to 100 mg/l):

   Pipette 10 ml, 30 ml, 50 ml, 60 ml, 80 ml, and 100 ml respectively of stock solution II (3.3.11) into a series of 100 ml volumetric flasks. Make up to volume with water.

The mass concentrations of chloride in these calibration solutions are 10 mg/l, 30 mg/l, 50 mg/l, 60 mg/l, 80 mg/l and 100 mg/l respectively. These calibration solutions are stable for one month.

c) Range I (100 mg/l to 1 000 mg/l):

Pipette 1 ml, 3 ml, 5 ml, 6 ml, 8 ml, and 10 ml respectively of stock solution I (3.3.10) into a series of 100 ml volumetric flasks. Make up to volume with water.

The mass concentrations of chloride in the resulting calibration solution are 100 mg/l, 300 mg/l, 500 mg/l, 600 mg/l, 800 mg/l and 1 000 mg/l respectively. These calibration solutions are stable for three months.

NOTE Other concentration ranges are applicable, provided they cover exactly one decade of concentration units.

3.4 Apparatus

3.4.1 Flow injection analysis system (FIA)

The flow injection system shall consist of the following basic components (see Figures B.1 and B.2).

3.4.1.1 **Reagent containers**.

3.4.1.2 **Low-pulse pump**.

3.4.1.3 **Calibrated chemically resistant pump tubes**, if required.

3.4.1.4 **Sample injection system** with an injection volume of 20 µl to 100 µl.

3.4.1.5 **Transport tubes** (internal diameter 0,5 mm to 0,8 mm), **tube connections and T-connections** of inert material and with minimum dead volumes.

3.4.1.6 **Photometer with flow cell**, wavelength range 450 nm to 480 nm.

3.4.1.7 **Registration unit** (e.g. strip chart recorder, integrator or printer/plotter).

In general, peak height signals are evaluated.

3.4.1.8 **Autosampler**, if required.

3.4.2 Continuous flow analysis system (CFA)

The continuous flow system shall consist of the following basic components (see Figures B.3 and B.4).

3.4.2.1 **Sampler** or other equipment which provides a reproducible sample and liquid transport.

3.4.2.2 **Reagent containers**.

3.4.2.3 **Low-pulse pump** with calibrated chemical resistant pump tubes.

3.4.2.4 **Inlet connector** made of glass or chemically resistant material, with reproducible air-, sample- and reagent segmentation, with calibrated transport tubes.

3.4.2.5 **Dialysis cell** (with a cellulose membrane, e.g. length 150 mm), if dilution or clean-up of samples is necessary.

3.4.2.6 **Photometer** with flow cell, wavelength range 450 nm to 480 nm.

3.4.2.7 Registration unit (e. g. strip chart recorder, integrator or printer/plotter).

In general peak height signals are evaluated.

3.4.2.8 Autosampler, if required.

NOTE In Figures B.3 and B.4, continuous flow systems with internal diameters of 2 mm (“macroflow”) are described. Similar systems with an internal diameter of 1 mm (”microflow”) are also allowable.

3.4.3 Additional apparatus

3.4.3.1 Graduated flasks, nominal capacity 100 ml, 200 ml and 1 000 ml.

3.4.3.2 Graduated pipettes, nominal capacity 1 ml to 100 ml.

3.5 Sampling and sample pretreatment

Store the samples in either glass or plastic containers for up to one month. Sample preservation is not required (see ISO 5667-3).

3.6 Procedure

3.6.1 Preparation of the measurement

a) Assemble the flow analysis system (FIA or CFA) in accordance with the flow diagrams (3.4.1, 3.4.2; Figures B.1 to B.4).

b) Before analysis, insert the tubes of the carrier solutions C1 to C3 (3.3.12, 3.3.13) and the reagent solution (3.3.9) into the appropriate canisters. Run the system for 10 min. Wait for a stable baseline and adjust the baseline to zero.

c) When the baseline shows no more drift, the system is ready for analysis. Check the reagent blank in accordance with 3.6.3 and calibrate in accordance with 3.6.4.

3.6.2 Quality requirements for the measuring system

3.6.2.1 Instrument performance check

The absorbance per centimetre of optical pathlength measured for the calibration solutions (3.3.14) shall be in the range from 0,03 to 2,0.

NOTE If the photometric detector does not give any absorbance readings, the absorbance may then be determined by comparison with an external absorbance-measuring spectrometer.

3.6.2.2 Daily sensitivity adjustment

If a recorder for the calculation of results is used, transfer the sample probe into a chloride calibration solution (3.3.14) with the highest concentration of the selected working range (10 mg/l, 100 mg/l or 1 000 mg/l, respectively). When there is a positive response at the registration unit due to the colour produced from the calibration solution, adjust the response to read about 95 % of full-scale deflection.

3.6.3 Checking the reagent blank

The reagent solution (3.3.9) shall not exceed an absorbance per centimetre of optical path length of 0,3. Otherwise consider the water as contaminated with chloride and take alternative steps. The absorbance can be measured by an external spectrometer.

3.6.4 Calibration

Prepare the required calibration solutions for each range according to 3.3.14.

Calibrate each range separately.

To start the calibration, position the output signal to zero.

Calibrate by sequentially applying the calibration solutions and reagent blanks.

Obtain the measured values corresponding to the calibration solutions applied.

The procedure for the calibration and the analysis of samples (3.6.5) shall be the same.

The following general equation (1) for the quadratic equation (see ISO 8466-2) shall apply.

$$y = c\rho^2 + b\rho + a \tag{1}$$

where

y is the measured value, in terms of instrument-related units (absorbance or a unit proportional to the absorbance);

ρ is the mass concentration, in milligrams per litre, of chloride in the calibration solutions;

a is the ordinate intercept of the calibration function, in terms of instrument-related units;

b is the parameter of the calibration function in terms of instrument-related units (l/mg);

c second-order parameter of the calibration function in terms of instrument-related units (l^2/mg^2).

3.6.5 Measurement

Analyse the samples in the same way as the calibration solutions with the flow analysis system FIA or CFA (3.4.1 or 3.4.2) respectively.

Dilute the sample, or use another working range, if the mass concentrations exceed the validity range of the selected working range.

Verify the validity of the calibration function of the selected working range after each sample series, at the most after 20 samples, using one calibration solution each for the lower and upper parts of the respective working range. If necessary recalibrate the system.

3.7 Calculation of results

Determine the mass concentration of chloride in the measuring solution using the measured value obtained as described in 3.6.5 from the calibration function (1) (3.6.4).

For the calculation use the appropriate calibration function. Do not extrapolate beyond the working range selected. Calculate ρ from equation (2):

$$\rho = -(b/2c) - \left[(b/2c)^2 - (a-y)/c\right]^{\frac{1}{2}} \tag{2}$$

For the explanation of the symbols in this equation, see 3.6.4, equation (1). All dilution steps shall be taken into account in the calculation.

4 Determination of chloride by flow analysis (FIA and CFA) with potentiometric detection

4.1 Principle

For FIA the sample is injected, via an injection valve, into a carrier stream. For CFA the sample is mixed with a carrier stream. The carrier stream containing the sample is mixed with a buffer solution. The chloride ions are determined by a specific chloride-ion-selective electrode (with a reference electrode) in a flowcell [7], [8], [9], [10].

4.2 Interferences

Ions that form insoluble substances with silver (Br^-, I^-, S^{2-}) or ions that form complexes with silver ions (CN^-, $S_2O_3^{2-}$) interfere with this method.

If sulfides are expected, 0,5 ml of hydrogen peroxide (3.3.7) per 100 ml of the water sample should be added. The mixture can be analysed after 5 min.

If Br^-, I^-, CN^- ions are expected up to a concentration of 0,1 g/l, mix the sample (1:2) with a solution containing 14,4 g of potassium bromate (4.3.3) and 76 ml of nitric acid II (4.3.4) in 1 000 ml of water. After 10 min the sample can be analysed.

4.3 Reagents

4.3.1 General

See 3.3.1. In addition to the reagents listed in 3.3 the following reagents of ”analytical grade quality” are required.

4.3.2 Potassium nitrate, KNO_3.

4.3.3 Potassium bromate, $KBrO_3$.

4.3.4 Nitric acid II, $c(HNO_3) = 1$ mol/l.

4.3.5 Carrier solution for the FIA method for ranges I to III (C4 in Figure B.5).

If there are no interfering ions (see 4.2) present in the sample, use water as carrier solution C4. If there are interfering ions (see 4.2) present in the sample, make up the carrier solution C4 as follows:

In a 1 000 ml volumetric flask dissolve 7,2 g of potassium bromate (4.3.3) and 38 ml of nitric acid II (4.3.4) in approximately 800 ml of water. Make up to volume with water.

This solution shall be prepared fresh daily.

4.3.6 Ionic strength adjustment buffer (ISA) solution for FIA (P1 in Figure B.5)

4.3.6.1 FIA ISA solution for samples *without* interfering ions (see 4.2)

a) For ranges III and II (1 mg/l to 10 and 10 mg/l to 100 mg/l chloride):

   In a 1 000 ml volumetric flask dissolve 3 ml of nitric acid II (4.3.4) and 10,1 g of potassium nitrate (4.3.2) in approximately 800 ml of water. Make up to volume with water.

   This solution may be stored for one month.

b) For range I (100 mg/l to 1 000 mg/l):

In a 1 000 ml volumetric flask dissolve 50,5 g of potassium nitrate (4.3.2) and 3 ml of nitric acid II (4.3.4) in approximately 800 ml of water. Make up to volume with water.

This solution may be stored for one month.

4.3.6.2 **FIA ISA solution for samples with interfering ions** (4.2) in the range (1 mg/l to 1 000 mg/l Cl^-)

In a 1 000 ml volumetric flask dissolve 7,2 g of potassium bromate (4.3.3) and 38 ml of nitric acid II (4.3.4) in approximately 800 ml of water. Make up to volume with water.

This solution shall be prepared fresh daily.

4.3.7 **Ionic strength adjustment buffer (ISA) solution for CFA** (P2 in Figure B.6) for all ranges (1 mg/l to 1 000 mg/l chloride).

4.3.7.1 CFA ISA for samples *without* interfering ions (4.2)

In a 1 000 ml volumetric flask dissolve 3 ml of nitric acid II (4.34) and 50,5 g of potassium nitrate (4.3.2) in approximately 900 ml of water, add 1 ml of detergent solution (3.3.8) and fill to the mark with water.

This solution may be stored for one month.

4.3.7.2 CFA ISA for samples *with* interfering ions (4.2)

In a 1 000 ml volumetric flask dissolve 38 ml of nitric acid II (4.3.4), and 7,2 g of potassium bromate (4.3.3) in approximately 900 ml of water, add 1 ml of detergent solution (3.3.8) and make up to volume with water.

This solution shall be prepared fresh daily.

4.4 Apparatus

4.4.1 Flow analysis system (FIA and CFA)

The flow injection system or the continuous flow system, respectively, consists of the components outlined in 3.4.1 or 3.4.2. (See Figures B.5 and B.6, and also Note in 3.4.2.8).

Instead of a photometer, a specific chloride-ion-selective electrode with a reference electrode and a millivoltameter with high impedance inlet (> 1 MΩ) are required.

4.4.2 Additional apparatus

The requirements given in 3.4.3 apply.

4.5 Sampling

The requirements given in 3.5 apply.

4.6 Procedure

4.6.1 Preparation of the measurement

Before starting the analysis, stabilize the baseline by pumping the required solutions (4.3.5, 4.3.6, 4.3.7) through the system for approximately 10 min.

When the baseline shows no more drift, the system is ready for sample analysis.

4.6.2 Quality requirements for the measuring system

a) Ranges I and II:

For calibration solution series (3.3.14) with mass concentrations of 10 mg/l and 100 mg/l, and of 100 mg/l and 1 000 mg/l, the potential difference shall be at least 55 mV.

b) Range III:

For calibration solutions (3.3.14) with mass concentrations of 1 mg/l and 10 mg/l, the potential difference shall be at least 25 mV.

4.6.3 Calibration

After testing the flow-through system (see 4.4.1) position the output signal, as specified by the manufacturer, to zero.

Choose the appropriate range (I, II or III) and prepare the calibration solutions (3.3.14). Calibrate each range separately.

Calibrate by sequentially applying the calibration solutions and reagent blanks [instead of a sample water (3.3.1) is used].

Obtain the measured values corresponding to the calibration solutions used by the manufacturer's specified procedure, as long as it matches the procedure described in this International Standard.

The test conditions for the calibration and the measurement of samples (3.6.5) shall be the same. The magnitude of the measurement signal is a function of the mass concentration of chloride. The following general equations (3) and (4) shall be used. For the use of a combined range of 10 mg/l to 1 000 mg/l, see annex C.

a) Range III (1 mg/l to 10 mg/l):

$$y = c\rho^2 + b\rho + a \tag{3}$$

b) Ranges I (100 mg/l to 1 000 mg/l) and II (10 mg/l to 100 mg/l):

$$y = d \lg \rho + e \tag{4}$$

where

y, ρ, a, b, c see 3.6.4

e is the ordinate intercept of the calibration function (4), in terms of instrument-related units;

d is the slope of the logarithmic calibration curve (4).

If the calibration solutions (3.3.14) are diluted previous to the calibration [e.g. by in-line dialysis, see Figure B.6 b)] the effective chloride concentration shall be considered for the choice of the suitable equation (3) or (4).

EXAMPLE If calibration solutions of range II (10 mg/l to 100 mg/l) are diluted 1:10 by an in-line dialyser, equation (3) should be used.

4.6.4 Measurement

Analyse the samples in the same way as the calibration solutions with the flow system (4.41).

Dilute the sample or use another working range if the mass concentrations exceed the validity range of the selected working range.

After each series of samples, but at least after 20 samples, run a low and a high calibration standard within the selected working range to check the validity of the calibration function. If necessary recalibrate the system.

4.7 Calculation of results

Determine the mass concentration of chloride in the sample solution using the measured value obtained as described in 4.6.4 from the calibration function (3) or (4) (4.6.3).

For calculation of results, use the appropriate calibration function. Do not extrapolate beyond the working range selected.

If potassium bromate (4.3.3) and nitric acid II (4.3.4) were added to the sample (see 4.2, 4.3.5 and 4.3.6.2), determine the potential signal of the reagent blank (see 4.6.3, third paragraph) separately and subtract it from the measured value y [equation (3) or (4)].

Calculate ρ from equation (5) or (6):

a) Range III (1 mg/l to 10 mg/l)

$$\rho = -(b/2c) - \left[(b/2c)^2 - (a-y)/c\right]^{\frac{1}{2}} \tag{5}$$

b) Ranges I (100 mg/l to 1 000 mg/l) and II (10 mg/l to 100 mg/l)

$$\lg \rho = (y-e)/d \quad \text{or}$$

$$\rho = 10^{(y-e)/d} \tag{6}$$

If the samples were diluted prior to the measurement [e.g. by in-line dialysis, see Figure B.6 b)] choose equation (5) or (6) appropriate to the effective chloride concentration of the diluted sample;

If a combined range 10 mg/l to 1 000 mg/l was used, consider annex C.

For the explanation of the symbols in these equations refer to 4.6.3, equations (3) and (4). All dilution steps shall be taken into account in the calculation.

5 Expression of results

Report the results in milligrams per litre (mg/l) or in grams per litre (g/l) to at most two significant figures.

EXAMPLE: Chloride: 17 mg/l

1,2 g/l

$5,4 \times 10^2$ mg/l

6 Test report

The test report shall refer to this International Standard and contain at least the following information:

a) identity of the water sample;

b) outline of the procedure used;

c) description of the sample preparation;

d) description of the equipment used ;

e) results (in accordance with clause 5);

f) any conditions which may have affected the results.

Annex A
(informative)

Performance characteristics

The statistical data in Tables A.1 to A.3 were established in an interlaboratory trial carried out by DIN in November 1996.

The following symbols are used:

p	is the number of laboratory sets;
n	is the number of outlier-free individual analytical values;
o	is the relative portion of the outliers, in percent;
μ	is the true value, by convention;
x	is the total mean;
RR	is the recovery rate, in percent;
s_r	is the estimate of the repeatability standard deviation;
CV_r	is the repeatability coefficient of variation;
s_R	is the estimate of the reproducibility standard deviation;
CV_R	is the reproducibility coefficient of variation;

Table A.1 — Statistical data for the determination of chloride with continuous flow analysis (CFA) and photometric detection, in accordance with ISO 5725-2

Sample No.	Type of matrix	p	n	o %	μ[d] mg/l	x mg/l	RR %	s_r mg/l	VC_r %	s_R mg/l	VC_R %
1	Water [a]	9	24	25	4,91	4,89	100	0,069	1,42	0,115	2,35
2	Surface water [b]	10	32	20	142,5	137,5	97	1,311	0,95	3,131	2,28
3	Waste water [c]	9	28	22,2	4 100	3 904	95	29,15	0,75	85,78	2,20

[a] Water in accordance with grade 1 of ISO 3696, spiked with chloride solution.

[b] River Rhine water.

[c] Industrial waste water (chemical industry).

[d] The true values μ were obtained by ion chromatography in accordance with ISO 10304-1 or ISO 10304-2.

Table A.2 — Statistical data for the determination of chloride with flow injection analysis (FIA) and photometric detection, in accordance with ISO 5725-2

Sample No.	Type of matrix	p	n	o %	μ^{d} mg/l	x mg/l	RR %	s_r mg/l	VC$_r$ %	s_R mg/l	VC$_R$ %
1	Water [a]	12	45	0	4,91	4,886	100	0,117	2,4	0,236	4,82
2	Surface water [b]	10	34	10,5	142,5	136,1	96	1,087	0,80	3,279	2,41
3	Waste water [c]	11	36	0	4 100	3 893	95	25,6	0,66	68,99	1,77

[a] Water in accordance with grade 1 of ISO 3696, spiked with chloride solution.

[b] River Rhine water.

[c] Industrial waste water (chemical industry).

[d] The true values μ were obtained by ion chromatography in accordance with ISO 10304-1 or ISO 10304-2.

Table A.3 — Statistical data for the determination of chloride with flow analysis systems (CFA, and FIA) and potentiometric detection, in accordance with ISO 5725-2

Sample No.	Type of matrix	p	n	o %	μ^{d} mg/l	x mg/l	RR %	s_r mg/l	VC$_r$ %	s_R mg/l	VC$_R$ %
1	Water [a]	8	28	0	4,91	4,806	98	0,060	1,26	0,151	3,14
2	Surface water [b]	8	28	0	142,5	135,3	95	1,816	1,34	4,014	2,97
3	Waste water [c]	8	28	0	4 100	3 888	94,8	43,69	1,12	109,7	2,82

[a] Water in accordance with grade 1 of ISO 3696, spiked with chloride solution.

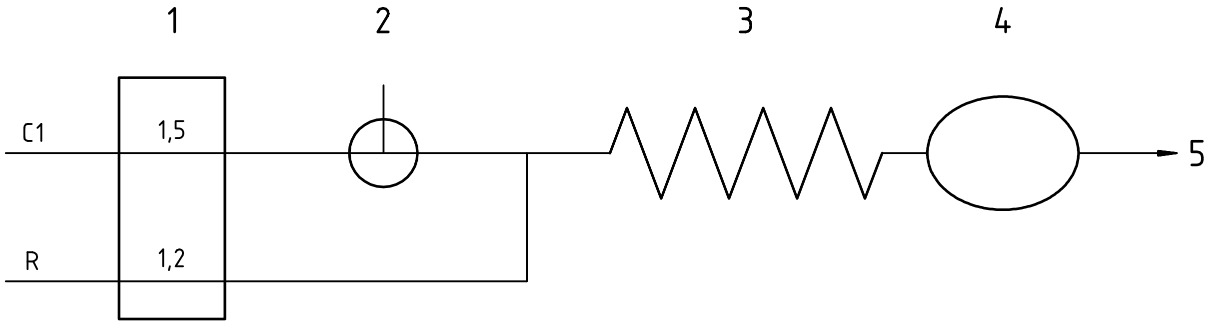
[b] River Rhine water.

[c] Industrial waste water (chemical industry).

[d] The true values μ were obtained by ion chromatography in accordance with ISO 10304-1 or ISO 10304-2.

Annex B
(informative)

Examples of flow diagrams



Key

1 Pump (flowrate, ml/min)

2 Injector (injection volume 100 µl)

3 Reaction coil (length 30 cm, internal diameter 0,5 mm)

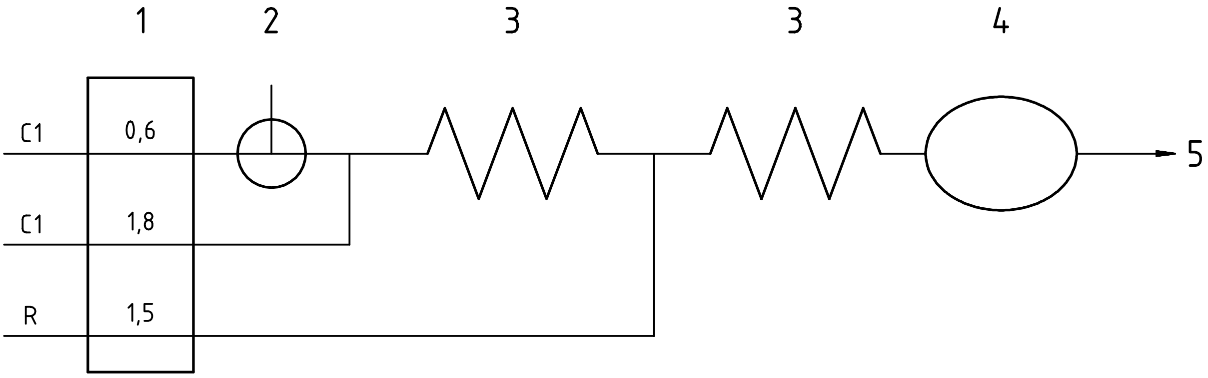
4 Detector (wavelength 450 nm to 480 nm)

5 Waste

C1 Carrier solution 1 (3.3.12) = water

R Reagent solution (3.3.9)

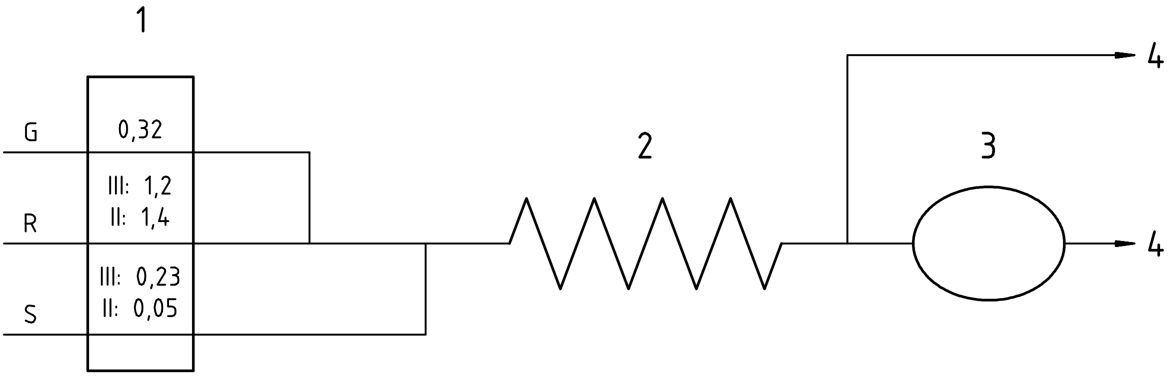
Figure B.1 — Example of a flow diagram for the determination of chloride, range 1 mg/l to 10 mg/l, by FIA and photometric detection (3.4.1)



Key

- II Working range II = 10 mg/l to 100 mg/l chloride
- I Working range I = 100 mg/l to 1 000 mg/l chloride
- 1 Pump (flowrate, ml/min)
- 2 Injector (injection volume: 50 µl for working range II, 20 µl for working range I)
- 3 Reaction coil (length 30 cm, internal diameter 0,5 mm)
- 4 Detector (wavelength 450 nm to 480 nm)
- 5 Waste
- C1 Carrier solution 1 (3.3.12) = water
- R Reagent solution (3.3.9)

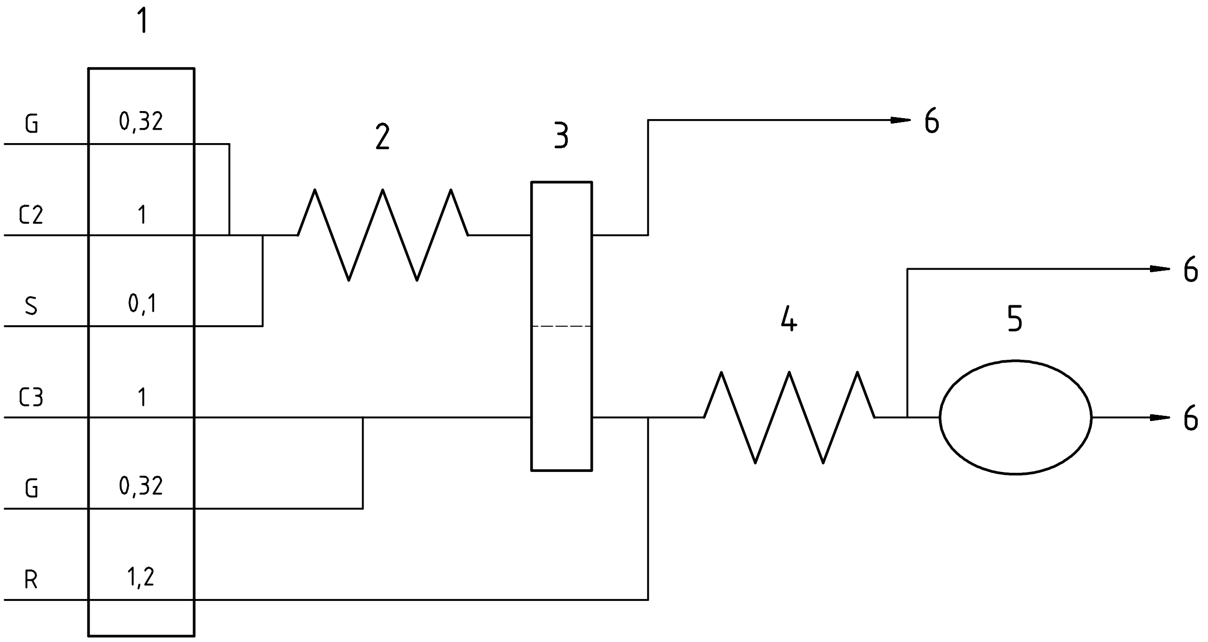
Figure B.2 — Example of a flow diagram for the determination of chloride, range 10 mg/l to 1 000 mg/l, by FIA and photometric detection (3.4.1)



Key

- III Working range III = 1 mg/l to 10 mg/l chloride
- II Working range II = 10 mg/l to 100 mg/l chloride
- 1 Pump (flowrate, ml/min)
- 2 Reaction coil (length 120 cm, internal diameter 2 mm)
- 3 Detector (wavelength 450 nm to 480 nm)
- 4 Waste
- G Segmentation gas (air)
- S Sample
- R Reagent solution (3.3.9)

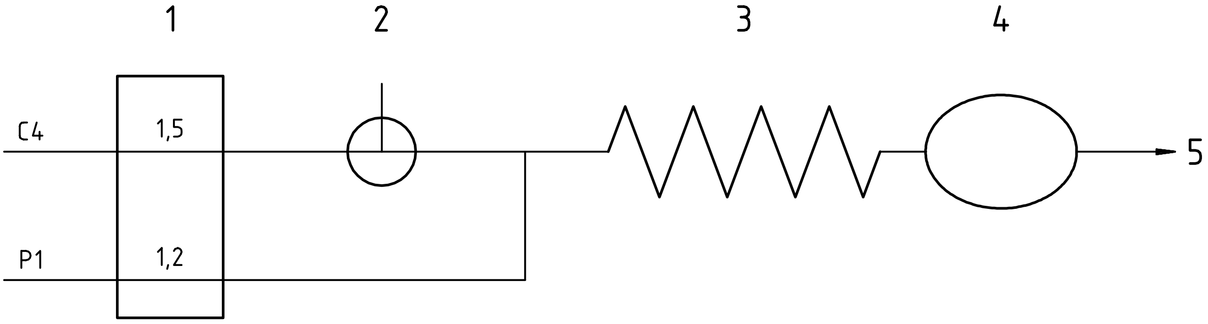
Figure B.3 — Example of a flow diagram for the determination of chloride, range 1 mg/l to 100 mg/l, by CFA and photometric detection (3.4.2)



Key

1	Pump (flowrate, ml/min)
2	Reaction coil (length 30 cm, internal diameter 2 mm)
3	Dialyser (length approximately 15 cm)
4	Reaction coil (length 120 cm, internal diameter 2 mm)
5	Detector (wavelength 450 nm to 480 nm)
G	Segmentation gas (air)
S	Sample
R	Reagent solution (3.3.9)
C2	Carrier solution 2 (3.3.13)
C3	Carrier solution 3 (3.3.13)

Figure B.4 — Example of a flow diagram for the determination of chloride, range 100 mg/l to 1 000 mg/l, by CFA and photometric detection (3.4.2)

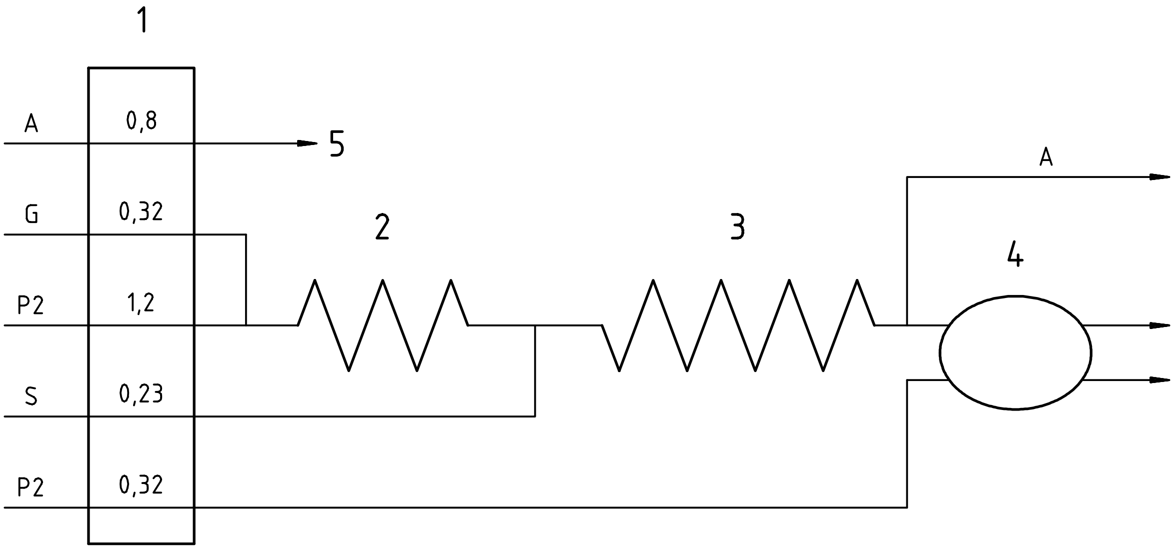


Calibration function:	use equation (3) for the range 1 mg/l to 10 mg/l; use equation (4) for the ranges 10 mg/l to 100 mg/l and 100 mg/l to 1 000 mg/l.
Calculation of results:	use equation (5) for the range 1 mg/l to 10 mg/l; use equation (6) for the ranges 10 mg/l to 100 mg/l and 100 mg/l to 1 000 mg/l.

Key

III	Working range III = 1 mg/l to 10 mg/l
II	Working range II = 10 mg/l to 100 mg/l
I	Working range I = 100 mg/l to 1 000 mg/l
1	Pump (flowrate, ml/min)
2	Injector (injection volume: 40 µl for working range I, 100 µl for working ranges II and III)
3	Reaction coil (length 60 cm, internal diameter 0,5 mm)
4	Ion-selective detector with reference electrode
5	Waste
P1	Ionic strength adjustment buffer (ISA) solution (4.3.6)
C4	Carrier solution (4.3.5)

Figure B.5 — Example of a flow diagram for the determination of chloride in the range 1 mg/l to 1 000 mg/l by FIA and potentiometric detection (4.4.1)



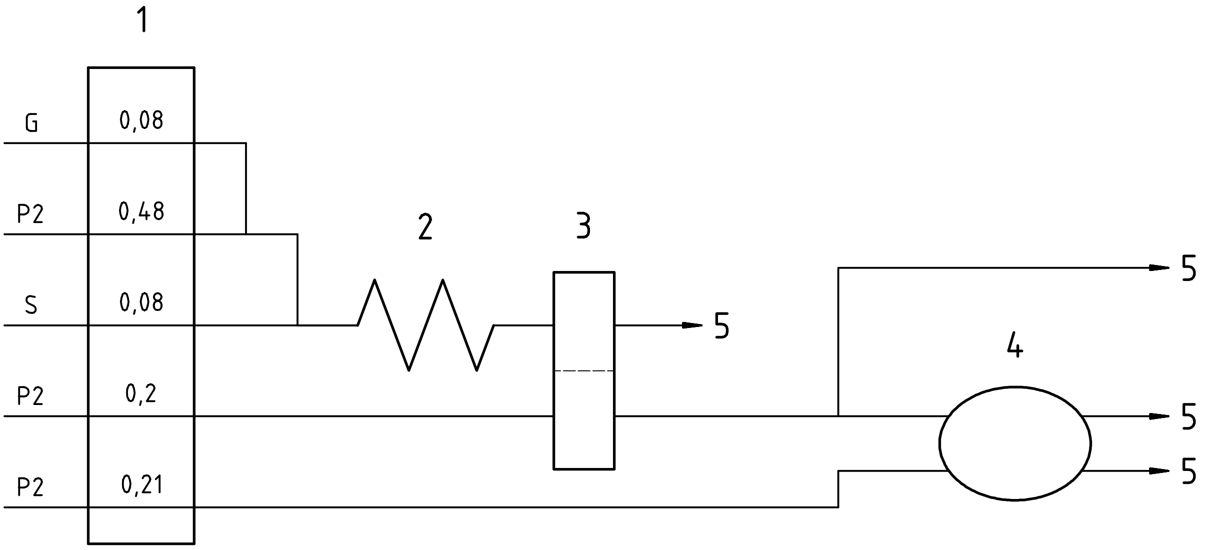
For all ranges:	1 mg/l to 1 000 mg/l
Calibration function:	use equation (3) for the range 1 mg/l to 10 mg/l; use equation (4) for the ranges 10 mg/l to 100 mg/l and 100 mg/l to 1 000 mg/l.
Calculation of results:	use equation (5) for the range 1 mg/l to 10 mg/l; use equation (6) for the ranges 10 mg/l to 100 mg/l and 100 mg/l to 1 000 mg/l.

Key

1	Pump (flowrate, ml/min)
2	Reaction coil (length 25 cm, internal diameter 2 mm)
3	Reaction coil (length 50 cm, internal diamter 2 mm)
4	Ion-selective detector with reference electrode
G	Segmentation gas (air)
S	Sample
P2	Ionic strength adjustment buffer (ISA) solution (4.3.7)
A	Transport of the reaction mixture to waste

a) “Macroflow” system for the range 1 mg/l to 1 000 mg/l

Figure B.6 — Examples of a flow diagram for the determination of chloride by CFA and potentiometric detection (4.4.1)



Calibration function: use equation (3)
Calculation of results: use equation (5)

Key

1	Pump (flowrate, ml/min)
2	Reaction coil (length 50 cm, internal diameter 1 mm)
3	Dialyser (length approximately 15 cm)
4	Ion-selective detector with reference electrode
5	Waste
G	Segmentation gas (air)
S	Sample
P2	Ionic strength adjustment buffer (ISA) solution (4.3.7)

b) “Microflow” system for the range 10 mg/l to 100 mg/l

Figure B.6 — Examples of a flow diagram for the determination of chloride by CFA and potentiometric detection (4.4.1)

Annex C
(informative)

Determination of chloride by flow analysis (FIA and CFA) and potentiometric detection with a single calibration function for the range 10 mg/l to 1 000 mg/l

C.1 General

With a certain loss of accuracy, instead of the two working ranges I (100 mg/l to 1 000 mg/l) and II (10 mg/l to 100 mg/l) a combined range of 10 mg/l to 1 000 mg/l can be applied. In this case, the method described in clause 4 of this International Standard can be applied with the following alterations.

C.2 Calibration solutions

The calibration solutions should cover a working range of 10 mg/l to 1 000 mg/l. They are prepared by diluting the stock solutions I or II (3.3.10 or 3.3.11). At least 10 calibration solutions (each concentration decade should contain the same number of solutions) are recommended. As an example, if 11 calibration solutions are applied proceed as follows:

Pipette 10 ml, 30 ml, 50 ml, 60 ml, 80 ml and 100 ml respectively of stock solution II (3.3.11), and 3 ml, 5 ml, 6 ml, 8 ml and 10 ml of stock solution I (3.3.10) into a series of 100 ml volumetric flasks. Make up to volume with water.

The mass concentrations of chloride in the resulting calibration solutions are 10 mg/l, 30 mg/l, 50 mg/l, 60 mg/l, 80 mg/l, 100 mg/l, 300 mg/l, 500 mg/l, 600 mg/l, 800 mg/l and 1 000 mg/l respectively. For stability of these calibration solutions, see 3.3.14.

NOTE The concentrations 10 mg/l, 30 mg/l, 50 mg/l, 60 mg/l, 80 mg/l and 100 mg/l respectively belong to the working range II; the concentrations 100 mg/l, 300 mg/l, 500 mg/l, 600 mg/l, 800 mg/l and 1 000 mg/l respectively belong to the working range I. Each working range is covered by six different concentration values.

C.3 Calibration

See 4.6.3.

Use equation (4) for the range of 10 mg/l to 1 000 mg/l chloride.

C.4 Determination

See 4.7.

Use equation (6) for the range of 10 mg/l to 1 000 mg/l chloride.

C.5 Examples of flow diagrams

See Figures B.5 and B.6. The flowrates, or the injection volumes, need to be changed slightly.

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Annex ZA (normative)
Normative references to international publications with their relevant European publications

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

NOTE Where an International Publication has been modified by common modifications, indicated by (mod.), the relevant EN/HD applies.

Publication	Year	Title	EN	Year
ISO 3696	1987	Water for analytical laboratory use - Specification and test methods	EN ISO 3696	1995

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