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Water quality — Determination of alkalinity —

Part 1:
Determination of total and composite alkalinity

Qualité de l'eau — Détermination de l'alcalinité —
Partie 1: Détermination de l'alcalinité totale et composite

Reference number
ISO 9963-1:1994(E)

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.

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.

International Standard ISO 9963-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods*.

ISO 9963 consists of the following parts, under the general title *Water quality — Determination of alkalinity*:

- *Part 1: Determination of total and composite alkalinity*
- *Part 2: Determination of carbonate alkalinity*

Annex A of this part of ISO 9963 is for information only.

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Water quality — Determination of alkalinity —

Part 1:
Determination of total and composite alkalinity

1 Scope

This part of ISO 9963 specifies a method for the titrimetric determination of alkalinity. It is intended for the analysis of natural and treated water, and waste water, and can be used directly for waters having an alkalinity concentration of up to 20 mmol/l. For samples containing higher concentrations of alkalinity, a smaller test portion can be used for analysis. The recommended lower limit is 0,4 mmol/l. Suspended matter in the form of carbonate may interfere with the analysis. This interference can be reduced by filtration prior to the titration.

The endpoint detection, using a pH-meter, is less prone to interferences than the use of the indicator.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 9963. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 9963 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

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

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

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

ISO 6107-2:1989, *Water quality — Vocabulary — Part 2.*

IEC 746-2:1982, *Expression of performance of electrochemical analyzers — Part 2: pH Value.*

3 Definitions

For the purposes of this part of ISO 9963, the following definitions apply.

3.1 alkalinity (A): The quantitative capacity of aqueous media to react with hydrogen ions. [ISO 6107-2]

3.2 methyl red (methyl orange) endpoint alkalinity: An arbitrary measurement of the total alkalinity (A_T) of water obtained by titration to the methyl red (methyl orange) indicator endpoint (pH 4,5); to assess the equivalent hydrogen carbonate, carbonate and hydroxide concentration of water.

3.3 phenolphthalein endpoint alkalinity; composite alkalinity (A_P)**:** The measurement by titration to the phenolphthalein endpoint (pH 8,3) of that portion of alkalinity arbitrarily attributed to all the hydroxyl and half the carbonate content of a water. [ISO 6107-2]

NOTE 1 The alkalinity of water is primarily a function of the hydrogen carbonate, carbonate and hydroxide concentrations. Other buffering substances (X) such as ammonia, borate, phosphate, silicate and organic anions may be included in the determination.

$$A_P \approx c\left(\mathrm{CO_3^{2-}}\right) - c(\mathrm{CO_2aq}) + c(\mathrm{OH^-}) - c(\mathrm{H^+}) + c(\mathrm{X})$$

$$A_T \approx 2c\left(\mathrm{CO_3^{2-}}\right) + c(\mathrm{HCO_3^-}) + c(\mathrm{OH^-}) - c(\mathrm{H^+}) + c(\mathrm{X})$$

By definition, composite alkalinity is zero for waters which have a pH value of 8,3 or less.

4 Principle

The sample is titrated with standard acid solution to fixed pH endpoint values of 8,3 and 4,5. These endpoints, which are determined visually or potentiometrically, are the selected equivalence points for the determinations of the three principal components: hydrogen carbonate, carbonate and hydroxide. The pH 8,3 endpoint approximates to the equivalent concentrations of carbonate and carbon dioxide and represents the titration of approximately all the hydroxide and half of the carbonate present. The pH 4,5 endpoint approximates the equivalence point for hydrogen ion and hydrogen carbonate and allows for the determination of the total alkalinity of the sample.

NOTE 2 The equivalent point values depend on the ionic strength as well as the concentration of total inorganic carbon and may not always be optimum at the chosen endpoints.

Whilst methyl orange and methyl red have been commonly used in the past as indicators for the determination of total alkalinity, in practice the use of different indicator systems produce slightly different results in alkalinity titrations. For alkalinity determinations in accordance with this part of ISO 9963, the correct bromocresol green-methyl red indicator solution as defined in 5.6 should be used.

5 Reagents

Use only reagents of recognized analytical grade.

Commercially available, ready-made solutions may be used.

5.1 Water, grade 2 in accordance with ISO 3696, free of interfering concentrations of acid or alkali and with a conductivity of less than 0,1 mS/m.

5.2 Sodium carbonate, standard solution, $c(\mathrm{Na_2CO_3}) \approx 0{,}025$ mol/l.

Dry 3 g to 5 g of sodium carbonate ($\mathrm{Na_2CO_3}$) at 250 °C ± 10 °C for 4 h. Allow to cool in a desiccator. Dissolve 2,65 g ± 0,20 g (m, weighed to the nearest 0,001 g) in water and dilute in a volumetric flask to 1 000 ml.

This solution is stable for at least one month if stored in a refrigerator at 4 °C and 8 °C.

5.3 Hydrochloric acid, $c(\mathrm{HCl}) \approx 0{,}10$ mol/l.

Dilute 8,6 ml ± 0,1 ml of hydrochloric acid (1,16 g/ml) to 1 000 ml with water. Standardize this solution as follows, using either potentiometric (5.3.1) or visual endpoint detection (5.3.2).

5.3.1 Potentiometric detection.

Pipette 25,0 ml ± 0,1 ml (V_1) of the sodium carbonate solution (5.2) into a titration vessel and add 75 ml ± 5 ml of water (5.1). Place the vessel on a magnetic stirrer and dip into the solution a plastics-coated magnetic stirrer bar and electrodes previously connected to a calibrated pH-meter. Start the stirrer and stir at a rate at which a vortex is just not perceptible. Titrate with 0,10 mol/l hydrochloric acid solution (5.3) until the meter reads pH 4,5 ± 0,05. Note the volume V_2, in millilitres, of acid consumed.

5.3.2 Visual endpoint detection.

Pipette 25,0 ml ± 0,1 ml (V_1) of approximately 0,025 mol/l sodium carbonate solution (5.2) into a 250 ml Erlenmeyer flask, and add 75 ml ± 5 ml of water and 0,1 ml ± 0,02 ml of bromocresol green-methyl red indicator solution (5.6). Titrate with 0,10 mol/l hydrochloric acid solution (5.3) until the greenish-blue colour disappears. Note the volume V_2, in millilitres, of acid consumed.

5.3.3 Blank determination.

Using 100 ml ± 5 ml of water, carry out a blank determination according to the appropriate procedure (5.3.1 or 5.3.2) and note the volume V_3, in millilitres, of acid consumed.

5.3.4 Calculation of the amount-of-substance concentration of the hydrochloric acid.

$$c(\mathrm{HCl},1) = \frac{mV_1}{53{,}00(V_2 - V_3)}$$

where

$c(\mathrm{HCl},1)$ is the actual concentration, expressed in moles per litre, of the nominally 0,10 mol/l hydrochloric acid solution (5.3);

m is the mass, in grams, of sodium carbonate taken for the preparation of standard solution (5.2);

V_1 is the volume, in millilitres, of sodium carbonate standard solution (5.2) taken for titration (normally 25 ml);

V_2 is the volume, in millilitres, of hydrochloric acid solution (5.3) consumed in the titration of the sodium carbonate standard solution (5.2);

V_3 is the volume, in millilitres, of hydrochloric acid solution (5.3) consumed in the blank titration.

Standardize this solution at least weekly.

5.4 Hydrochloric acid, $c(\mathrm{HCl}) \approx 0{,}02$ mol/l.

Pipette 100 ml ± 1 ml of hydrochloric acid solution (5.3) into a 500 ml volumetric flask. Dilute to volume with water and mix well. Prepare freshly before use.

Calculate the amount-of-substance concentration as follows:

$$c(\mathrm{HCl},2) = 0{,}2 \times c(\mathrm{HCl},1)$$

where

$c(\mathrm{HCl},1)$ is the actual concentration, expressed in moles per litre, of the nominally 0,10 mol/l hydrochloric acid solution (5.3);

$c(\mathrm{HCl},2)$ is the actual concentration, expressed in moles per litre, of the nominally 0,02 mol/l hydrochloric acid solution (5.4).

5.5 Phenolphthalein indicator solution.

Dissolve 1,0 g ± 0,1 g of phenolphthalein in 100 ml ± 2 ml of ethanol [> 90 % (*V/V*) ethanol] and dilute with water to 200 ml ± 4 ml. Mix well.

5.6 Bromocresol green-methyl red indicator solution.

Dissolve 0,200 g ± 0,005 g of bromocresol green and 0,015 g ± 0,002 g of methyl red in 100 ml ± 4 ml of ethanol [> 90 % (*V/V*) ethanol]. Store in an amber glass bottle.

5.7 Sodium thiosulfate solution, $c(\mathrm{Na_2S_2O_3.5H_2O}) \approx 0{,}1$ mol/l.

Dissolve 2,5 g ± 0,2 g of sodium thiosulfate pentahydrate ($\mathrm{Na_2S_2O_3.5H_2O}$) in 100 ml ± 5 ml of water. Store in an amber glass bottle in the refrigerator for a maximum of six months.

6 Apparatus

Usual laboratory equipment and, in particular, the following should be used.

6.1 Magnetic stirrer, and plastics-coated stirring bar.

6.2 pH-meter, with a compatible electrode system suitable for the measurement of pH to within ± 0,05 pH units over the range 4 to 10, and a suitable titration vessel designed so that contact with air is minimized. The equipment shall be set up, calibrated (preferably using buffers with pH values 4, 7 and 9), and used according to IEC 746-2.

6.3 Precision burette, of capacity 10 ml, graduated in divisions of 0,02 ml, and conforming to the requirements of ISO 385-1.

7 Sampling and sample treatment

Collect samples in clean polyethylene or borosilicate glass bottles with a volume of at least 100 ml. Fill the bottle completely with the sample and insert the stopper so that no air remains inside the bottle. Ideally analyse the samples immediately after collection. If this is not possible, store in a cool place. In order to avoid nitrification or scaling. Many types of samples are little affected during storage. Test for any effects of storage on the type of samples analysed. (See ISO 5667-1 and ISO 5667-2.)

8 Procedure

Strongly coloured or turbid samples should be analysed by the potentiometric method.

8.1 Potentiometric method

Calibrate the pH-meter according to 6.2.

NOTE 3 The potentiometric titration is free from interference caused by oxidizing agents, although difficulties in endpoint detection may be experienced in the presence of organic substances. Soaps, oily substances, etc. may coat the glass electrode and cause a sluggish response. Additional time should be allowed between titrant additions to let the electrode come to equilibrium, and the electrodes should be cleaned frequently.

8.1.1 Determination of composite alkalinity titratable to pH 8,3 (phenolphthalein alkalinity)

NOTE 4 Absorption of atmospheric carbon dioxide during the titration of composite alkalinity can lower the results.

Pipette 100 ml ± 1 ml of sample (volume V_4) into the titration vessel. Place the vessel on a magnetic stirrer and dip a plastics-coated stirring bar and pH-electrodes into the solution. Start the stirrer motor and stir at a rate at which a vortex is just not perceptible. Measure the pH value of the sample and, if it is found to be 8,3 or less, record the composite alkalinity titratable to pH 8,3 as zero. If the alkalinity is in the range 4 mmol/l to 20 mmol/l, use 0,1 mol/l hydrochloric acid (5.3). If the alkalinity is in the range 0,4 mmol/l to 4 mmol/l, use 0,02 mol/l hydrochloric acid (5.4). Titrate the sample with the appropriate acid and note the volume V_5, in millilitres, of acid consumed.

Retain the solution for use in the determination of the total alkalinity.

8.1.2 Determination of total alkalinity

Continue to titrate the solution reserved from the determination of composite alkalinity titratable to pH 8,3 (see 8.1.1) with the appropriate hydrochloric acid solution until the meter reads pH 4,5 ± 0,05 (in the vicinity of pH 4,5, add the titrant drop by drop and allow at least 30 s for the electrodes to attain equilibrium with the solution). Note the total volume V_6, in millilitres, of acid required.

8.2 Visual method

NOTE 5 Remove any free chlorine present by adding 0,1 ml of sodium thiosulfate solution (5.7) per 200 ml of sample. This procedure removes up to 1,8 mg/l of chlorine.

8.2.1 Determination of composite alkalinity titratable to pH 8,3 (phenolphthalein alkalinity)

NOTE 6 Absorption of atmospheric carbon dioxide during the titration of composite alkalinity can lower the results.

Pipette 100 ml ± 1 ml of sample (volume V_4) into a 250 ml Erlenmeyer flask and add 0,1 ml ± 0,02 ml of phenolphthalein indicator solution (5.5). If a pink colour is not obtained, regard the composite alkalinity titratable to pH 8,3 as zero. Titrate pink-coloured samples with acid until the pink colour disappears. If the alkalinity is in the range 4 mmol/l to 20 mmol/l, use 0,1 mol/l hydrochloric acid (5.3). If the alkalinity is in the range 0,4 mmol/l to 4 mmol/l, use 0,02 mol/l hydrochloric acid (5.4). Note the volume V_5, in millilitres, of acid consumed.

Retain the solution for use in the determination of the total alkalinity.

8.2.2 Determination of total alkalinity

Add 0,1 ml ± 0,02 ml of bromocresol green-methyl red indicator solution (5.6) to the solution reserved from the determination of composite alkalinity titratable to pH 8,3 (see 8.2.1). Continue to titrate with the appropriate hydrochloric acid solution until the colour changes from greenish-blue to grey. Note the total volume V_6, in millilitres, of acid consumed.

9 Expression of results

9.1 Calculation

9.1.1 Composite alkalinity titratable to pH 8,3 (phenolphthalein alkalinity)

$$A_\mathrm{P} = \frac{c(\mathrm{HCl}) \times V_5 \times 1\ 000}{V_4}$$

where

A_P	is the capacity to react with hydrogen ions, expressed in millimoles per litre, of composite alkalinity titratable to pH 8,3;
$c(\mathrm{HCl})$	is the actual concentration, expressed in moles per litre, of the hydrochloric acid solution (5.3 or 5.4) used;
V_4	is the volume, in millilitres, of the test portion (normally 100 ml);
V_5	is the volume, in millilitres, of hydrochloric acid solution (5.3 or 5.4) consumed to reach pH 8,3.

9.1.2 Total alkalinity

$$A_\mathrm{T} = \frac{c(\mathrm{HCl}) \times V_6 \times 1\ 000}{V_4}$$

where

A_T	is the capacity to react with hydrogen ions, expressed in millimoles per litre, of total alkalinity titratable to pH 4,5;

$c(\text{HCl})$	is the actual concentration, expressed in moles per litre, of the hydrochloric acid solution (5.3 or 5.4) used;
V_4	is the volume, in millilitres, of the test portion (normally 100 ml);
V_6	is the volume, in millilitres, of hydrochloric acid solution (5.3 or 5.4) consumed to reach pH 4,5.

10 Test report

The test report shall include the following information:

a) a reference to this part of ISO 9963;

b) precise identification of the sample;

c) the results, expressed in millinoles (H^+) per litre;

d) any departure from the procedure specified or any other circumstance that may have affected the results.

Annex A
(informative)

Information on factors for the conversion of alkalinity values to alternative units

Alkalinity values may be expressed in alternative units. Factors for the conversion from millimoles per litre are given in table A.1.

Table A.1

Alternative unit for the expression of results	Conversion factor
mmol/l $CaCO_3$	0,50
mg/l $CaCO_3$	50
mg/l HCO_3^-	61
Parts/100 000	5,0
English degree (= 1 Clark degree)	3,50
German degree	2,80
French degree	5,0
U.S. degree	2,90

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