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Water quality — Determination of alkalinity —

Part 2:
Determination of carbonate alkalinity

Qualité de l'eau — Détermination de l'alcalinité —
Partie 2: Détermination de l'alcalinité carbonate

Reference number
ISO 9963-2:1994(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 9963-2 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*

Annexes A and B of this part of ISO 9963 are for information only.

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Water quality — Determination of alkalinity —

Part 2:
Determination of carbonate alkalinity

1 Scope

This part of ISO 9963 specifies a method for the titrimetric determination of carbonate alkalinity in natural and drinking water. Using a higher pH value for the endpoint than the method specified in ISO 9963-1, the influence of other hydrogen acceptors, such as anions of humic acids, is reduced by the procedure.

The method is intended for samples with a carbonate alkalinity between 0,01 mmol/l and 4 mmol/l (as H^+ equivalents). For samples containing higher concentrations of alkalinity, a smaller test portion can be used for analysis.

In this context, carbonate alkalinity is often called total alkalinity and usually has nearly the same numerical value as methyl orange alkalinity (MO-alkalinity).

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

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

ISO 9963-1:1994, *Water quality — Determination of alkalinity — Part 1: Determination of total and composite alkalinity.*

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

3 Definition

For the purposes of this part of ISO 9963, the following definition applies.

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

In this method, the endpoint is chosen in such a way as to permit the full neutralization of the carbonate system.

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

Usually proton acceptors (X) other than the carbonate system are present in low concentrations and can often be disregarded. Examples of such buffering substances are ammonia, phosphate, and anions of humic and other organic acids.

4 Principle

Alkalinity is determined by titration with hydrochloric acid, with simultaneous removal of carbon dioxide. In this way, a precise endpoint independent of the initial concentration of alkalinity can be used. The endpoint preferably needs to be as close to neutrality as possible but still low enough to allow the removal of carbon dioxide produced. In this part of ISO 9963, the endpoint is set at pH 5,4, since the pH value can easily be determined with the indicator chosen. The induced systematic error is corrected by titrating a blank.

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 Gas, free from carbon dioxide, nitrogen or alternatively a gas free from carbon dioxide obtained by passing air through a standing tube filled with soda lime or another compound that absorbs carbon dioxide. Then pass the gas through a wash bottle containing water and subsequently the gas distribution tube (see figure 1).

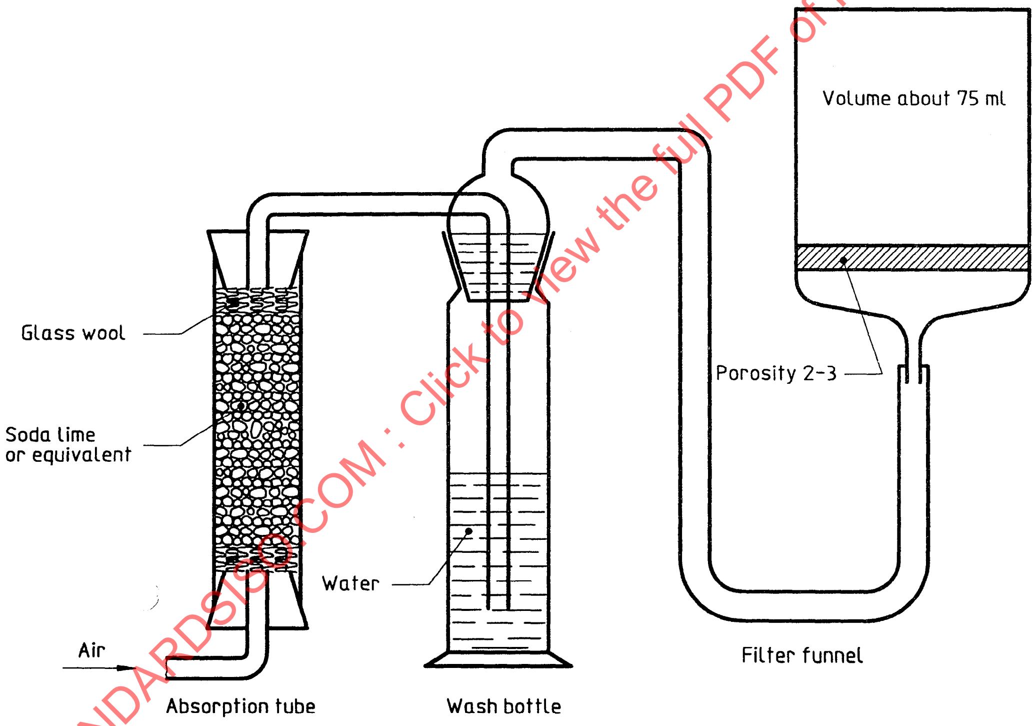

Figure 1 — Principle for absorption of carbon dioxide from air

5.3 Mixed indicator pH 5,4.

Dissolve 0,040 g ± 0,005 g of methyl red and 0,060 g ± 0,005 g of bromocresol green in 100 ml of ethanol [> 90 % (*V/V*)]. Neutralize the solution with about 2 ml of 0,1 mol/l sodium hydroxide until a brown colour appears. Check the neutrality of the indicator solution by titration to endpoint of one sample. If the brown colour does not remain after the addition of 10 more drops of the indicator, adjust the pH of the indicator solution. Stored in an amber glass bottle, the solution is stable for at least 6 months.

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

Dry sodium carbonate ($\mathrm{Na_2CO_3}$) in an oven at 250 °C ± 10 °C for 4 h. Allow to cool in a desiccator. Dissolve 1,3 g ± 0,1 g (weighed to the nearest 0,001 g) in water in a 500 ml volumetric flask.

This solution is stable for at least one month if stored in a refrigerator.

5.5 Hydrochloric acid, $c(\mathrm{HCl}) \approx 0{,}020$ mol/l.

Dilute 1,7 ml ± 0,1 ml of concentrated hydrochloric acid ($\rho \approx 1{,}18$ g/ml) to 1 000 ml with water in a volumetric flask.

An equivalent, commercially available solution can be used.

Standardize this solution at least weekly as follows.

Pipette 2,00 ml ± 0,02 ml of the sodium carbonate solution (5.4) into the titration vessel (6.2) and add 40 ml ± 5 ml of water (5.1). Titrate according to the procedure using electrodes (see 8.1) or with indicator (8.2) for the endpoint detection

Perform at least three titrations, and record the volumes (V_2) of hydrochloric acid consumed. The difference between the highest and lowest volume of hydrochloric acid consumed shall be less than 0,05 ml. Continue until three consecutive titrations give the required result. Using 50 ml ± 5 ml of water (5.1), carry out a blank determination in the same manner and note the volume V_3, in millilitres, of acid consumed.

Calculate the concentration of the hydrochloric acid using the equation

$$c(\mathrm{HCl}) = \frac{2mV_1}{53{,}00(V_2 - V_3)}$$

where

$c(\mathrm{HCl})$	is the concentration, expressed in moles per litre, of the hydrochloric acid solution (5.5);
m	is the mass, in grams, of sodium carbonate taken for the preparation of solution 5.4;
V_1	is the volume, in millilitres, of sodium carbonate solution (5.4) taken for titration (normally 2,0 ml);
V_2	is the volume, in millilitres, of hydrochloric acid solution (5.5) consumed in the titration of the sodium carbonate solution (5.4);
V_3	is the volume, in millilitres, of hydrochloric acid solution (5.5) consumed in the blank titration.

6 Apparatus

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

6.1 Burette, preferably of total capacity 10 ml, graduated in divisions of 0,02 ml, and conforming to the requirements of ISO 385-1.

6.2 Titration vessel, use either a glass filter funnel with a porosity of 2-3 and a volume of about 75 ml, or a gas distribution tube for dipping into the titration vessel (an Erlenmeyer flask with a volume of 100 ml).

6.3 pH-meter, with a compatible electrode system suitable for the measurement of pH to within ± 0,05 pH units over the range 3 to 10, for use when the endpoint determination is to be made using a pH-meter. The equipment shall be set up, calibrated, and used according to IEC 746-2.

Alternatively, a titrator fulfilling these specifications can be used.

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. Analyse the samples immediately after collection. If this is not possible, store the samples at a temperature of 4 °C to 8 °C in order to avoid nitrification or scaling. (See ISO 5667-2.)

8 Procedure

Mount the components according to figure 1.

NOTE 1 Coloured samples interfere with the indicator endpoint determination. Such samples should be analysed using a pH-meter.

8.1 Endpoint detection with a pH-meter

Set the gas flow (5.2) to the titration vessel (6.2) at a rate that produces abundant bubbles and transfer 50,0 ml ± 0,1 ml of sample (volume V_4) to the vessel. Insert the pH electrodes and titrate slowly with hydrochloric acid (5.5) to a pH value of 5,4. The pH value has to be stable for at least 30 s, if not continue the titration. Note the volume V_5, in millilitres, of acid consumed.

If the volume of acid consumed exceeds 10 ml, take a smaller volume of the sample (V_4) and dilute to 50 ml ± 5 ml with water (5.1). In this case, the volume of acid consumed shall be not less than 3 ml.

8.2 Endpoint detection with indicator

Set the gas flow (5.2) to the titration vessel (6.2) at a rate that produces abundant bubbles and transfer 50,0 ml ± 0,1 ml of sample (volume V_4) to the vessel. Add three drops of indicator and titrate slowly with hydrochloric acid (5.5) until the colour changes to grey with a trace of red. The colour has to remain for at least 30 s, if not continue the titration. Note the volume V_5, in millilitres, of acid consumed.

If the volume of acid consumed exceeds 10 ml, take a smaller portion of the sample and dilute to 50 ml ± 5 ml with water (5.1). In this case, the volume of acid consumed shall be not less than 3 ml.

8.3 Blank sample

Titrate 50 ml of water (5.1) in the same way as for the sample. Perform at least three titrations and calculate the mean value (volume V_6).

9 Expression of results

9.1 Calculation

Calculate the concentration of alkalinity, expressed in millimoles per litre, using the equation

$$A = \frac{c(\mathrm{HCl})\,(V_5 - V_6) \times 1\,000}{V_4}$$

where

A	is the alkalinity of the sample, expressed in millimoles per litre;
$c(\mathrm{HCl})$	is the concentration, expressed in moles per litre, of the hydrochloric acid (5.5);
V_4	is the volume, in millilitres, of the sample;
V_5	is the volume, in millilitres, of hydrochloric acid (5.5) consumed by the sample;
V_6	is the volume, in millilitres, of hydrochloric acid (5.5) consumed by the blank sample (8.3).

Report the result, expressed in millimoles per litre, to two significant digits.

9.2 Precision

Two interlaboratory tests performed in 1988 and 1992 gave the results shown in table 1.

In two international interlaboratory calibrations this method was used by one laboratory, with the results shown in table 2.

At one laboratory, a control solution with a concentration of 0,200 mmol/l gave a mean value of 0,201 mmol/l and a coefficient of variation of 2,0 % (number of measuring values = 49).

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 result, expressed in millimoles per litre to two significant digits;

d) the endpoint detection used;

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

Table 1 — Precision data

Type of water	**Reference**	**Number of laboratories**	**Number of outliers**	**Mean concentration** mmol/l	**Coefficient of variation** %
Drinking water	SNV 3535	70 69 69	2 3 4	2,984 4,480 0,933	3,6 3,6 4,0
Natural water	ITM 1993	100 101 100 101	2 1 1 1	1,142 0,884 1,406 1,188	3,4 3,4 3,0 3,5

Table 2 — Comparison of results using this method with other methods for the determination of alkalinity

Type of water	**Reference**	**Number of laboratories**	**Number of outliers**	**Concentration,** mmol/l	
				This method	All methods
9105 Sample A Sample B	NIVA 1991	20 20	1 1	0,298 0,358	0,300 0,358
9206 Sample A Sample B	NIVA 1992	20 20	13 13	0,042 0,151	0,047 0,155

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
English degree (= 1 Clark degree)	3,50
German degree	2,80
French degree	5,0
U.S. degree	2,90

Annex B
(informative)

Bibliography

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