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Water quality — Determination of total alkalinity in sea water using high precision potentiometric titration

Qualité de l'eau — Détermination de l'alcalinité totale dans l'eau de mer en utilisant une titration potentiométrique de haute précision

Reference number
ISO 22719:2008(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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 22719 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

The greenhouse effect, induced by anthropogenic carbon dioxide, CO_2, in the atmosphere is a serious global environmental issue. A key factor controlling the concentration of atmospheric CO_2 is its absorption into the ocean. Since the volume of ocean water is huge, the change in the oceanic carbonate system from year to year is slight, and it is necessary to measure its components continuously with great precision over a long period. Furthermore, the oceanic carbonate system is related to many components such as water temperature, salinity, dissolved oxygen, and nutrient elements.

The oceanic carbonate system can be depicted by measuring at least two parameters of four: total inorganic carbon; total alkalinity; fugacity of CO_2; and pH of sea water. At the time of publication, it is possible to determine the first two parameters more precisely for subsurface water. Analytical methods for sea water samples, however, require specific conditions and techniques essential to the precise and accurate determination. This International Standard describes a method for the determination of total alkalinity in sea water with an error of less than 0,1 %.

This method is designed to provide international compatibility of accurate data sets on total alkalinity in sea water, which are collected by various communities. Such compatibility is the basis for national and international operational observation and monitoring programs of the oceanic carbonate system, as well as individual research work.

INTERNATIONAL STANDARD **ISO 22719:2008(E)**

Water quality — Determination of total alkalinity in sea water using high precision potentiometric titration

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard 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 and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies an open-cell potentiometric titration determination of total alkalinity in sea water. The results are expressed in moles per kilogram of sea water. The method is suitable for assaying oceanic levels of total alkalinity (2 000 µmol kg^{-1} to 2 500 µmol kg^{-1}) for normal sea water of practical salinity ranging from 30 to 40.

2 Normative references

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

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

3 Terms and definitions

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

3.1
total alkalinity
A_T
⟨sea water⟩ number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant, $K \leqslant 10^{-4,5}$ at 25 °C and zero ionic strength) over proton donors (acids with $K > 10^{-4,5}$) in 1 kg of sample

NOTE This definition is taken from Reference [5].

3.2
practical salinity
S
⟨sea water⟩ the ratio K_{15} of the electrical conductivity of the sea water sample at the temperature of 15°C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 32,435 6 × 10^{-3}, at the same temperature and pressure

NOTE This definition is taken from Reference [6], p. 12, and was formulated and adopted by the UNESCO/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards, Sidney, B.C., Canada, September 1-5, 1980, and endorsed by those international bodies. As a ratio, the practical salinity has no unit.

4 Principle

A known amount of sea water is placed in an open cell where it is titrated in a two stage procedure with a solution of hydrochloric acid. The acid solution also contains sodium chloride to compensate for the sodium ion concentration of the sea water and to maintain approximately constant activity coefficients during the titration. An open cell is used so that, in subsequent data processing, it can be assumed that the total dissolved inorganic carbon (and hence the residual bicarbonate ion concentration) is approximately zero between pH 3,0 and pH 3,5. The progress of the titration is monitored using a pH glass-reference cell, and the total alkalinity is computed from the titrant volume and electromotive force (EMF) measurements using a non-linear least-squares approach allowing for the reactions of hydrogen ion with sulfate and fluoride ions.

5 Apparatus

The setup of apparatus specified in 5.2 and 5.4 is shown in Figure 1.

Usual laboratory equipment, and in particular the following.

5.1 Sampling equipment.

5.1.1 For laboratory use.

5.1.1.1 Calibrated balance, capable of weighing 200 g to within ± 0,01 g.

5.1.1.2 Plastic screw-cap bottle, of capacity 125 ml, with cap.

5.1.2 For use on board ship, preferably a **volumetric dispensing system**, containing a constant volumetric pipette made of glass with valves at each end, maintained at constant temperature by an air bath or a water jacket. The sample water — maintained at the same temperature — is flushed into the pipette using pressurised air. A constant volume of water is dispensed by switching the valve. The temperature of the sample water shall be known to within ± 0,4 °C.

A **manual pipette** may be used on condition that the temperature of sample water and room air is strictly controlled.

5.2 Titration cell assembly.

5.2.1 Jacketed beaker, of capacity 200 ml. A glass beaker enclosed by a water jacket (Figure 1), of internal diameter 57 mm.

5.2.2 Calibrated thermometer, readable to 0,01 °C, used to confirm that the solution temperature remains constant to within ± 0,05 °C during the titration and to provide the value of solution temperature for use in subsequent calculations.

5.2.3 Water bath, capable of being maintained at a constant temperature to within ± 0,05 °C.

5.2.4 Magnetic stirrer, of dimensions 38 mm × 8 mm.

5.2.5 Holder for burette tip, electrode, and thermometer

5.3 EMF-measuring assembly.

5.3.1 Digital voltmeter, readable to 0,01 mV.

5.3.2 High-impedance voltage follower amplifier system, used to buffer the EMF of the glass electrode-reference cell so that it can be measured accurately using the digital voltmeter.

NOTE A digital pH meter (± 0,1 mV) can be used instead of a digital voltmeter and voltage-follower amplifier, but with a loss in precision.

5.3.3 pH glass-reference electrode

A very rapid response pH glass electrode system in sea water is essentially important. The 90 % response time during a pH change of 0,1 should be less than 10 s when sea water is titrated by acid titrant. To reduce the sample volume, the combination of a pH glass-reference electrode is more suitable.

The performance of the pH electrode is paramount for achieving high quality results. The performance of a new electrode can be assessed by measuring A_T on a sea water reference material. If the certified value is not obtained, it may be necessary to replace the electrode.

5.4 Burette assembly.

A highly reproducible burette (± 0,001 ml) is necessary to obtain the highest quality results. Unfortunately, although the burette is capable of the high reproducibility needed, its accuracy is typically not as good, and the burette system shall be calibrated prior to use.

5.4.1 Automatic burette, of capacity 5 ml ± 0,002 ml, equipped with an anti-diffusion tip.

5.4.2 Calibrated thermometer, readable to 0,1 °C, used to measure acid temperature.

5.5 Miscellaneous.

5.5.1 Transfer device for samples by mass, designed to allow dispensation from a bottle with a greased ground-glass joint in a manner that ensures that grease is not transferred to the weighing bottle. Such a system may comprise a rubber stopper to which two rigid plastic tubes are skewered; the rubber stopper is secured to the sample bottle with a metal clamp. Connected tubes should be chemically inert and acid resistant. One of the tubes is long enough to make contact with the bottom of a 500 ml sample bottle, and the other tube protrudes about 6 mm below the stopper. The shorter tube is attached with about 500 mm of tubing to a rubber bulb, which is used to pressurise the system. The other tube is attached to a length of tubing (approx. 500 mm) and is closed with a pinch clamp. This tube is used to dispense the sample.

5.5.2 Basin for waste.

5.5.3 Wash bottle, containing water (6.2).

6 Reagents

6.1 Titrant, calibrated solution for normal sea water samples, containing hydrochloric acid, 0,1 mol/kg, and sodium chloride, 0,6 mol/kg.

Ideally, the hydrochloric acid titrant solution is calibrated with an accuracy of better than ± 0,02 % using a coulometric titration procedure (see e.g. Reference [7]). In addition, the density of this titrant solution should be known as a function of temperature with an accuracy of better than ± 0,02 % experimentally by using a pyknometer (e.g. ISO 758). However, these procedures are complicated and require a great deal of skill. Furthermore, acid concentration and density may be changed by evaporation in several days. It is necessary to recalibrate the acid from time to time. Thus, the calibration of acid titrant using certified reference material (CRM) is recommended (see B.1.3).

6.2 Deionised ultrapure water, of resistivity about 18 MΩ cm.

7 Procedure

7.1 Sampling

Collect the sea water sample according to the standard method for water sampling of dissolved gases (see ISO 5667-1). It is strongly recommended that the sample is analysed within a few hours. When analysis is not possible immediately after sampling, add mercury(II) chloride. Recommended minimum amount is about 0,02 % by volume of saturated aqueous solution. Store the samples in a cool, dark place (preferably refrigerated, but not frozen) until use.

WARNING — Dispose of samples containing mercury(II) chloride in accordance with local government regulations.

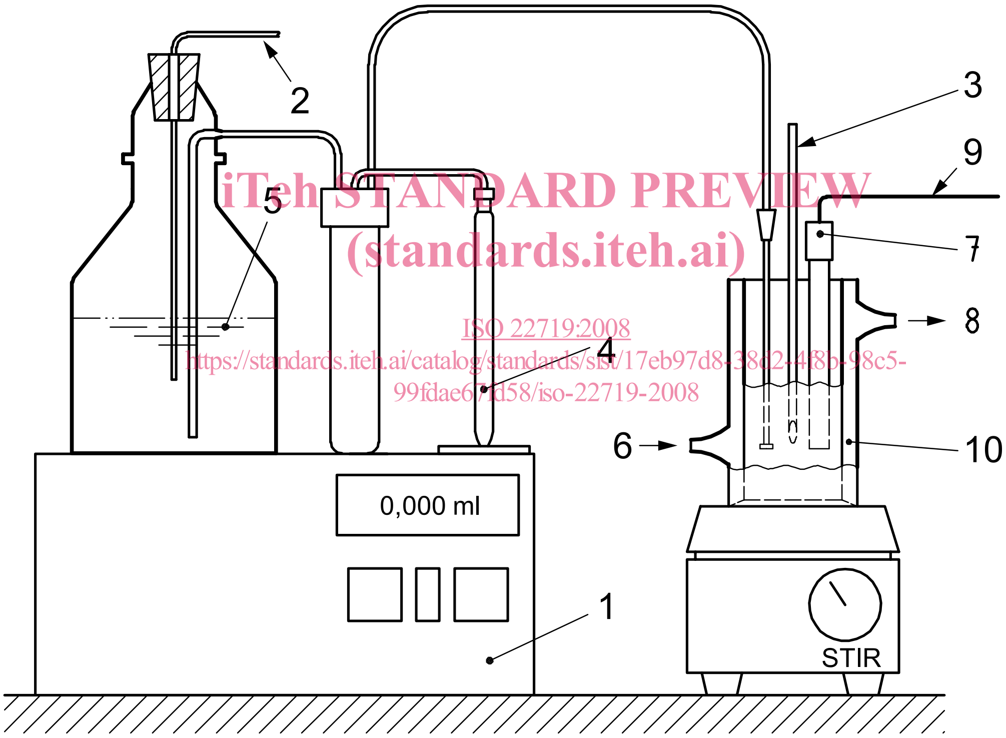
7.2 Equipment setup

Assemble the apparatus as shown in Figure 1.

Use extra caution when assembling the burette glass pieces and tubing. Make all connections finger tight, and do not overtighten. The most common cause of leaks and bubbles is damaged threads and chipped glass.

Set the water bath to a suitable temperature (close to room temperature).

Mix the hydrochloric acid titrant solution to ensure a consistent temperature and composition.



Key

1	automatic burette
2	sensor for thermometer
3	thermometer
4	burette reservoir
5	HCl/NaCl titrant
6	inlet from water bath
7	combination electrode
8	outlet to water bath
9	lead to EMF-measurement system
10	jacketed beaker

Figure 1 — Open-cell alkalinity measurement setup

Ensure that the automatic burette and tubing are thoroughly flushed with the titrant solution and that there are no air bubbles present.

IMPORTANT — If the system has not been used for some time, it may be necessary to condition the pH glass-reference cell. This can be achieved by carrying out a titration whose result is discarded. (This first measurement is often a little lower than the correct value.)

7.3 Sample transfer

7.3.1 Preparation of sample

Bring the sample to the required testing temperature; thoroughly mix the content of the sample bottle.

Remove the stopper of the bottle and use tissue paper to remove as much grease as possible.

7.3.2 Sampling by mass in the laboratory

Dry the longer tube of the sample transfer device (5.5.1); insert it into the sample bottle, securing it with the metal clamp.

Pressurise the bottle, and flush the tubing with about 20 ml of sample (discard to waste).

Fill a plastic bottle (5.1.1.2) with sample, cap tightly, and weigh (5.1.1.1); record the mass to the nearest 0,01 g.

Carefully pour the sample into the clean 250 ml jacketed beaker containing a 38 mm stir bar.

Recap the plastic bottle, and record the empty mass. The sample mass is obtained by difference.

7.3.3 Sampling by volume on board ship

Maintain the sample water and pipette at the same temperature and record it to the nearest 0,1 °C.

Draw up a known volume of sample water using the exactly calibrated automatic volumetric dispensing system or manual pipette (5.1.2). Record the volume, for later conversion to mass using an expression for the density of sea water at a known salinity and temperature.

Dispense the sample water into a clean 250 ml jacketed beaker containing a 38 mm stir bar.

7.4 Titration procedure

Purge the remaining acid in the burette (from the previous titration) into the waste basin, and refill the burette. To prevent the forming of bubbles in the burette and tubing, vent the acid bottle during each filling of the burette.

Record the hydrochloric acid solution temperature to the nearest 0,1 °C.

Rinse the acid tip, electrode, and thermometer thoroughly with water from the wash bottle. Gently touch dry with tissue paper.

Position the holder assembly over the beaker such that three parts dip into the sample without interfering with the stir bar.

With slow stirring, dispense enough hydrochloric acid to bring the sample to just above pH 3,5.

NOTE The volume dispensed depends on the alkalinity of the sample and the sample size.

Increase the stirring rate until it is quite vigorous, but not splashing.