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Water quality — Determination of pH_t in sea water — Method using the indicator dye *m*-cresol purple

Qualité de l'eau — Détermination du pH_t dans l'eau de mer — Méthode utilisant l'indicateur coloré au pourpre de m*-crésol*

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Foreword

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The committee responsible for this document is 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 one of the serious global environmental issues. A key factor controlling the atmospheric CO_2 is its absorption into the ocean. As a result of the absorption, the pH in the upper layer of the ocean is observed to have fallen gradually, and its influence on the living organisms is a matter of concern all over the world.

On the other hand, carbon capture and storage (CCS) technology is considered as a useful means of reducing the CO_2 emissions from fossil fuel. When ocean environment such as sub-seabed aquifer is selected as a storage site, the monitoring of carbonate system including pH in sea water becomes very important. The analytical method for pH_t in sea water (the total hydrogen ion concentration pH scale) samples requires specific conditions and techniques essential to the precise and accurate determination. This International Standard describes a method for the determination of pH_t in sea water with the repeatability less than 0,003.

This method will provide international communities accurate data sets on pH_t in sea water being compatible with each other. This is the base of national and international operational observation or monitoring programs of the oceanic carbonate system as well as individual research works.

Water quality — Determination of pH$_t$ in sea water — Method using the indicator dye *m*-cresol purple

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International 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 in accordance with this International Standard be carried out by suitably qualified staff.

1 Scope

This International Standard specifies a spectrophotometric determination of the pH$_t$ of sea water on the total hydrogen ion concentration pH scale using the indicator dye *m*-cresol purple. The total hydrogen ion concentration, $[H^+]_t$, is expressed as moles per kilogram of sea water. The method is suitable for assaying oceanic levels of pH$_t$ 7,4 to 8,2 for normal sea water of practical salinity ranging from 20 to 40.

2 Terms and definitions

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

2.1
total hydrogen ion concentration $[H^+]_t$

hydrogen ion concentration including the contribution of the hydrogen sulfate ions in the sea water

Note 1 to entry: Total hydrogen ion concentration is defined as:

$$[\mathrm{H}^+]_\mathrm{t} = [\mathrm{H}^+]_\mathrm{F}\left(1 + S_\mathrm{T} / K_\mathrm{S}\right) \approx [\mathrm{H}^+]_\mathrm{F} + [\mathrm{HSO}_4^-]$$

where

$[H^+]_F$ is the free concentration of hydrogen ion in sea water;

S_T is the total sulfate concentration $\left(\left\lfloor \mathrm{HSO}_4^- \right\rfloor + \left\lfloor \mathrm{SO}_4^{2-} \right\rfloor\right)$;

K_S is the acid dissociation constant for HSO_4^-.

The pH$_t$ is then defined as the negative of the base 10 logarithm of the hydrogen ion concentration as:

$$\mathrm{pH}_\mathrm{t} = -\log_{10}\left(\frac{[\mathrm{H}^+]_\mathrm{t}}{\mathrm{mol/kg}}\right)$$

2.2
practical salinity

S

ratio K_{15} of the electrical conductivity of the sea water sample at the temperature of 15 °C on IPTS-68 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

3 Principle

The values of pH_t are determined by adding an indicator to sea water. For the sulfonephthalein indicators such as *m*-cresol purple, the reaction of interest at sea water pH_t is the second dissociation as given in Formula (1):

$$\mathrm{HI^-}(\mathrm{aq}) = \mathrm{H^+}(\mathrm{aq}) + \mathrm{I^{2-}}(\mathrm{aq}) \tag{1}$$

where I represents the indicator, which is present at a low level in a sea water sample. The total hydrogen ion concentration of the sample can then be determined as given in Formula (2):

$$\mathrm{pH_t} = \mathrm{p}K\left(\mathrm{HI^-}\right) + \log_{10}\frac{\left[\mathrm{I^{2-}}\right]}{\left[\mathrm{HI^-}\right]} \tag{2}$$

The principle of this approach uses the fact that the different forms of the indicator have substantially different absorption spectra. Thus the information contained in the composite spectrum can be used to estimate $[I^{2-}]/[HI^-]$.

At an individual wavelength, λ, the measured absorbance, A_λ, in a cell with a pathlength L is given by the Beer-Lambert law as:

$$\frac{A_\lambda}{L} = \varepsilon_\lambda\left(\mathrm{HI^-}\right)\left[\mathrm{HI^-}\right] + \varepsilon_\lambda\left(\mathrm{I^{2-}}\right)\left[\mathrm{I^{2-}}\right] + B_\lambda + \mathrm{e} \tag{3}$$

where B_λ corresponds to the background absorbance of the sample and e is an error term due to instrumental noise. Provided that the values of the extinction coefficients: ε_λ (HI^-) and ε_λ (I^{2-}) have been measured as a function of wavelength, absorbance measurements made at two or more wavelengths can be used to estimate the ratio $[I^{2-}]/[HI^-]$.

In the case that only two wavelengths are used, and provided that the background can be eliminated effectively by a subtractive procedure, Formula (3) can be rearranged to give (assuming no instrumental error):

$$\frac{\left[\mathrm{I^{2-}}\right]}{\left[\mathrm{HI^-}\right]} = \frac{A_1/A_2 - \varepsilon_1\left(\mathrm{HI^-}\right)/\varepsilon_2\left(\mathrm{HI^-}\right)}{\varepsilon_1\left(\mathrm{I^{2-}}\right)/\varepsilon_2\left(\mathrm{HI^-}\right) - A_1/A_2\varepsilon_2\left(\mathrm{I^{2-}}\right)/\varepsilon_2\left(\mathrm{HI^-}\right)} \tag{4}$$

where the numbers 1 and 2 refer to the wavelengths chosen. For the best sensitivity, the wavelengths corresponding to the absorbance maxima of the base (I^{2-}) and acid (HI^-) forms, respectively, are used. The various terms ε are the extinction coefficients of the specified species at wavelengths 1 and 2, respectively.

4 Reagents

Use only reagents of recognized analytical grade.

4.1 ***m*-cresol purple**, containing no spectrophotometrical impurities.

NOTE 1 Reference [14] showed that the indicator can be characterized and purified using the HPLC system. The wavelength of isosbestic point for HI^-/I^{2-} of the pure *m*-cresol purple, $\lambda_{isos}(HI^-/I^{2-})$ depends on the following formula: $\lambda_{isos}(HI^-/I^{2-}) = 490{,}6 - 0{,}10\ t$, where t is the temperature in degrees Celsius. That for H_2I/HI^-, it is also $\lambda_{isos}(H_2I/HI^-) = 482{,}6 - 0{,}10\ t$.

NOTE 2 References [14] and [17] describe the purification method of *m*-cresol purple.

4.2 Solution of pure *m*-cresol purple.

A concentrated (at least 2 mmol/l) pure indicator solution of known pH adjusted to be in the range 7,9 ± 0,1 pH units, chosen to match pH_t measurements from an oceanic profile, is required; this implies that for *m*-cresol purple A_1/A_2 approximately 1,6.

NOTE The absorbance ratio of a concentrated indicator solution can be measured using a cell with a short pathlength (0,5 mm).

4.3 Deionized ultrapure water, of resistivity about 18 MΩ cm.

5 Apparatus

Usual laboratory equipment and, in particular, the following:

5.1 Flexible drawing tube

Approximately 40 cm long, sized to fit snugly over cell port. Silicone rubber is suitable. The drawing tube can be pre-treated by soaking in clean sea water for at least one day. This minimizes the amount of bubble formation in the tube when drawing a sample.

5.2 Spectrophotometric cell

These should be made of optical glass with a 10 cm pathlength, two ports and polytetrafluoroethylene stoppers. A sufficient number of cells are needed to collect all the samples that will be analysed from a particular cast.

NOTE A flow through cuvette with a 10 cm pathlength is also available. Sample bottles of at least 200 ml with air tight caps are needed to use the cuvette.

5.3 Micropipette

A micropipette is used to add the indicator to the cell. It should be of ~0,1 cm^3 capacity with a narrow polytetrafluoroethylene (PTFE) tube attached to act as a nozzle.

5.4 High-quality spectrophotometer

For work of the highest sensitivity and precision, a double-beam spectrophotometer is desirable. However, good results can be obtained with a high-quality single-beam instrument.

5.5 Temperature-control system for spectrophotometer cell

Commercially manufactured, thermostated spectrophotometer compartments that can accommodate 10 cm cells are rarely available and one will probably have to be custom-made. The temperature should be regulated to within 0,1 °C.

5.6 System to warm samples to measurement temperature

Although, it is possible to warm up the cells containing samples in the sealed bags in a thermostat bath, this is inconvenient. It is much better to build a custom-made thermostated compartment that can hold approximately 12 cells at once without getting them wet.

5.7 Thermostat bath

Temperature ±0,05 °C, to regulate the temperature of the cell compartment and the temperature of the system.