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

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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*.

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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.

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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:

$$[H^+]_t = [H^+]_F \left(1 + S_T / K_S\right) \approx [H^+]_F + [HSO_4^-]$$

where

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

S_T is the total sulfate concentration $\left(\left[HSO_4^-\right] + \left[SO_4^{2-}\right]\right)$;

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:

$$pH_t = -\log_{10}\left(\frac{[H^+]_t}{\text{mol/kg}}\right)$$

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

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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):

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

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):

$$pH_t = pK\left(HI^{-}\right) + \log_{10}\frac{\left[I^{2-}\right]}{\left[HI^{-}\right]} \quad (2)$$

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:

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

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):

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

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.

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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.

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6 Sampling

Collection of water at sea from the water sampler bottle must be done soon after opening the sampler and before much other water has been removed from it. This is necessary to minimize exchange of CO_2 with the air space in the sampler which affects all carbon parameters except total alkalinity. It is desirable that the carbon samples be collected before the sampler bottle is half empty and within 10 min of it being first opened.

Rinse the sample bottle — If the bottle is not already clean, rinse it twice with 30 cm to 50 cm of sample to remove any traces of a previous sample.

Fill the sample bottle — Fill the bottle smoothly from the bottom using a drawing tube which extends from the sampler bottle drain to the bottom of the sample bottle. It is critical to remove any bubbles from the draw tube before filling. Overflow the water by at least a full bottle volume. The air space with the sample bottle is kept to a minimum.[9][10]It is allowed to draw the sample directly from sampler bottle into the optical cell with two ports.

It is recommended that the pH analysis must be performed immediately after sampling, although storage experiments showed that the pH of sea water is stable within 24 h even in the case of coastal water (see Annex B). However, while awaiting analysis, store the samples in the refrigerator or icebox (not frozen).

7 Procedure

In the case of optical cell with two ports, warm sample cell to (25,0 ± 0,1) °C by placing a number of cells in a thermostated compartment (see 5.6) for a few hours. Place the cell in the thermostated sample compartment of the spectrophotometer by cleaning and drying the exterior of the cell.

Measure and record the absorbances at three wavelengths: at the wavelengths corresponding to the absorption maxima of the base (I^{2-}) and acid (HI^{-}) forms of the *m*-cresol purple, 578 nm and 434 nm, respectively, and a non-absorbing wavelength (730 nm).

Remove one of the cell caps to inject *m*-cresol purple. Add approximately 0,05 cm^3 to 0,1 cm^3 of *m*-cresol purple to the sample, replace the cap and shake the cell to mix the sea water and *m*-cresol purple. The amount of *m*-cresol purple required is that which will produce absorbance values of between 0,4 and 1,0 at each of the two absorbance peaks.

Return the cell to the spectrophotometer, again measure and record the absorbances at three wavelengths of sea water after adding *m*-cresol purple.

Cells should be positioned to maintain consistent alignment(s) between two absorbance measurements.

NOTE In the case of flow through cuvette, warm pH sample bottles to (25,0 ± 0,1) °C and measure and record the reference absorbances at three wavelengths as described above. Mix lightly the measure amount of sea water and *m*-cresol purple in such a way that absorbance values are between 0,4 and 1,0 at each of the two absorbance peaks. Again measure and record the absorbances at three wavelengths of sea water after adding *m*-cresol purple immediately.

For routine samples, single measurement is sufficient. Multiple measurement of reference material is recommended for checking precision and accuracy of the method.

8 Calculation and expression of results

8.1 Correction of measured absorbances

At each of the three wavelengths, subtract the absorbances measured for the background measurement (without indicator) from the corresponding absorbances measured for the system containing indicator.

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In addition, the absorbance measured at a non-absorbing wavelength is used to monitor and correct for any baseline shift due to error in repositioning the cell, instrumental shifts, etc. This assumes that the magnitude of any observed baseline shift is identical across the visible spectrum. Subtract the measured shift from the background-corrected absorbances at wavelengths 1 and 2 to obtain the final corrected absorbance value at each wavelength. These final absorbance values, corrected for background absorbances and any observed baseline shifts, are used to calculate A_1/A_2, the absorbance ratio which describes the extent of protonation of the indicator.

The difference between the baseline absorbance (sea water only) and the absorbance of the sample and indicator at 730 nm should be no greater than ±0,001. If this value is exceeded, the cell should be removed and the optical windows cleaned before the absorbances are measured again.

8.2 Calculation of the pH_t of the sea water and indicator

The pH_t of the sea water and indicator in the cell is computed from:

$$pH_t = pK\left(HI^-\right) + \log_{10}\left(\frac{A_1/A_2 - \varepsilon_1\left(HI^-\right)/\varepsilon_2\left(HI^-\right)}{\varepsilon_1\left(I^{2-}\right)/\varepsilon_2\left(HI^-\right) - A_1/A_2\varepsilon_2\left(I^{2-}\right)/\varepsilon_2\left(HI^-\right)}\right) \qquad (5)$$

Formula (5) can be written in a form with fewer parameters:

$$pH_t = -\log 10\left\{K_2\varepsilon_1\left(I^{2-}\right)/\varepsilon_2\left(HI^-\right)\right\} + \log_{10}\left(\frac{A_1/A_2 - \varepsilon_1\left(HI^-\right)/\varepsilon_2\left(HI^-\right)}{1 - A_1/A_2\varepsilon_2\left(I^{2-}\right)/\varepsilon_1\left(I^{2-}\right)}\right) \qquad (6)$$

where K_2 is the equilibrium constant between the species HI^- and I^{2-} (expressed on the total hydrogen ion concentration scale in mol/kg), and A_1 and A_2 are the corrected absorbances measured at the wavelengths corresponding to the absorbance of 578 nm and 434 nm, respectively.

The first term of Formula (6), $-\log_{10}\{K_2\varepsilon_1(I^{2-})/\varepsilon_2(HI^-)\}$, is a function of salinity and temperature and has been determined by careful laboratory measurements.

$$-\log_{10}\{K_2\varepsilon_1(I^{2-})/\varepsilon_2(HI^-)\} = a + b/T + c\ln T - dT$$

where parameters of a, b, c and d are in the range of $278{,}15 \leq T \leq 308{,}15\ K$ and $20 \leq S \leq 40$.

$a = -246{,}642\,09 + 0{,}315\,971\,S + 2{,}885\,5 \times 10^{-4}\,S^2$

$b = 7\,229{,}238\,64 - 7{,}098\,137\,S - 0{,}057\,034\,S^2$

$c = 44{,}493\,382 - 0{,}052\,711\,S$

$d = 0{,}078\,134\,4$

The various extinction coefficient terms ε correspond to values measured for the specified species at wavelengths 578 nm and 434 nm and are defined as follows:

$$\varepsilon_1(HI^-)/\varepsilon_2(HI^-) = -0{,}007\,762 + 4{,}517\,4 \times 10^{-5}\,T$$

$$\varepsilon_2(I^{2-})/\varepsilon_1(I^{2-}) = -0{,}020\,813 + 2{,}602\,62 \times 10^{-4}\,T + 1{,}043\,6 \times 10^{-4}\,(S - 35)$$

NOTE The $-\log_{10}\{K_2\varepsilon_1(I^{2-})/\varepsilon_2(HI^-)\}$ given here and the various extinction coefficient terms ε are those from Reference [14].

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8.3 Correction for pH_t change resulting from addition of the indicator

The addition of indicator to the sea water sample will perturb the pH_t (another acid–base system has been added). Although, care is taken to minimize this (by adjusting the indicator solution pH), it is desirable to correct for the addition of indicator to obtain the best pH_t measurements.

Although, in principle, the pH_t perturbation could be calculated from knowledge of the equilibrium chemistry of the sample and the indicator, it is simpler to evaluate the magnitude of the correction empirically. A pair of additions of indicator is made to each of a series of sea water samples with different pH_t values, and the change in the measured ratio (A_1/A_2) with the second addition of indicator solution is determined as a function of the measured value (A_1/A_2) determined after the first addition of indicator using a least squares procedure.

$$\frac{\Delta\left(A_1 / A_2\right)}{V} = \mathrm{a} + \mathrm{b}\left(A_1 / A_2\right) \tag{7}$$

where V is the volume of indicator added at each addition. The final, corrected, absorbance ratio is given in Formula (8):

$$(A_1/A_2)_{\mathrm{corr}} = (A_1/A_2) - V[\mathrm{a} + \mathrm{b}(A_1/A_2)] \tag{8}$$

NOTE Absorbance at the isosbestic point wavelength for HI^-/I^{2-} depends on the concentration of indicator. Then, $(A_1/A_2)_{\mathrm{corr}}$ can be determined by the linear regression of (A_1/A_2) and the absorbance at the isosbestic point wavelength.

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Annex A
(informative)

Performance data

An interlaboratory trial was organized by Dr. Shuichi Watanabe and supervised by Dr. Koh Harada, Convenor of ISO/TC 147/SC 2/WG 67 with the assistance of Dr. Yoshiyuki Nakano and Mr. Koichi Goto and was performed in Spring 2014. A total of 11 laboratories from 8 countries participated (Japan: 3, France: 2, Canada: 1, Korea: 1, Norway: 1, Portugal: 1, Sweden: 1, UK: 1). Two participants did not adhere to the method description. Their results were excluded from the statistical evaluation of the interlaboratory trial.

Five bottles of 500 ml sea water sample which were subsampled from one large container were sent to each laboratory. The sea water was collected in the western North Pacific and its salinity was 34,399.

The results are given in Table A.1.

Table A.1 — Performance data for sea water pH

Sample	**Matrix**	l	n	o %	$\bar{\bar{x}}$	X	η %	s_R	$C_{V,R}$ %	s_r	$C_{V,r}$ %
1	Sea water	8	107	11,1	7,992	—	—	0,003	0,040	0,002	0,030

l number of laboratories after outlier rejection

n number of analytical results after outlier rejection

o percentage of outliers

$\bar{\bar{x}}$ overall mean of results (without outliers)

X assigned value

η recovery rate

s_R reproducibility standard deviation

$C_{V,R}$ coefficient of variation of reproducibility

s_r repeatability standard deviation

$C_{V,r}$ coefficient of variation of repeatability

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Annex B
(informative)

Storage stability

The storage stability of sea water sample for pH_t was confirmed by sequential experimentation over 24 h. Sea water samples were collected at the coastal sea of Aomori Prefecture, Japan by a plastic bucket. Salinity of the sea water was 33,532. Sea water samples 1 were sampled in 250 ml glass bottles from a bucket. Samples 2 were filtered through 25 mm-diameter Whatman GF/F filter in laboratory and sampled in 250 ml glass bottles. Samples 3 were sampled in 250 ml glass bottles from a bucket and poisoned with 100 µl of over saturated solution of mercury chloride. These samples were stored in a refrigerator and got out an hour and a half before analysis.

The results are given in Table B.1.

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Table B.1 — Storage stability of sea water pH_t

Sample	Matrix	Date Time dd hh:mm	pH_t at 25 °C
1	Sea water	16 13:29	7,953
1	Sea water	16 13:48	7,955
1	Sea water	16 16:07	7,953
1	Sea water	16 18:14	7,952
1	Sea water	17 09:55	7,950
1	Sea water	17 12:40	7,952
1	Sea water	17 15:03	7,953
Average			7,952
Standard deviation			0,001
2	Filtrated sea water	16 16:24	7,941
2	Filtrated sea water	16 16:32	7,942
2	Filtrated sea water	16 18:32	7,941
2	Filtrated sea water	17 10:12	7,939
2	Filtrated sea water	17 12:58	7,932
2	Filtrated sea water	17 15:22	7,938
2	Filtrated sea water	17 17:34	7,940
Average			7,939
Standard deviation			0,003
3	Sea water + $HgCl_2$	16 13:40	7,953
3	Sea water + $HgCl_2$	16 13:56	7,952
3	Sea water + $HgCl_2$	16 16:15	7,956
3	Sea water + $HgCl_2$	16 18:24	7,956
3	Sea water + $HgCl_2$	17 10:04	7,955
3	Sea water + $HgCl_2$	17 12:48	7,956
3	Sea water + $HgCl_2$	17 15:14	7,953
Average			7,955
Standard deviation			0,002

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