SOP 6

Determination of the pH of sea water using a glass / reference electrode cell

1. Scope and field of application

This procedure describes a method for the potentiometric determination of the pH of seawater on the total hydrogen ion concentration pH scale. The total hydrogen ion concentration, $[H^+]$, is expressed as moles per kilogram of sea water.

2. Definition

The total hydrogen ion concentration of sea water includes the contribution of the medium ion sulfate and is defined as

$$[H^+] = [H^+]_F (1 + S_T / K_S)$$

$$\approx [H^+]_F + [HSO_4^-] \; ; \tag{1}$$

$[H^+]_F$ is the *free* concentration of hydrogen ion in sea water, S_T is the total sulfate concentration ($[HSO_4^-] + [SO_4^{2-}]$) and K_S is the acid dissociation constant for HSO_4^-. The pH is then defined as the negative of the base 10 logarithm of the hydrogen ion concentration:

$$pH = -\log\left(\frac{[H^+]}{mol \cdot kg\text{-soln}^{-1}}\right). \tag{2}$$

3. Principle

Values of pH are determined experimentally from sequential measurements of the e.m.f. (E) of the cell

reference electrode	concentrated KCl solution	test solution	glass (H^+) electrode
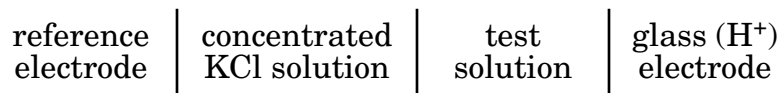
in a standard buffer (S) of known (defined) pH and in the sea water sample (X).

The operational pH is defined by the expression

$$pH\,(X) = pH(S) + \frac{E_S - E_X}{RT\,\ln 10/F} \quad . \tag{3}$$

Residual liquid-junction error is minimized by matching the composition of the standard buffer to the sea water sample, *i.e.* by making the buffer up in synthetic sea water.

Values of pH(S) have been assigned to various standard buffers in synthetic sea water. These are based on careful laboratory measurements made using cells without liquid junction.

4. Apparatus

4.1 pH cell

A combination glass / reference electrode is typically the most convenient cell to use; however, measurement quality can often be improved by using separate glass and reference electrodes.

4.2 Voltmeter with high input impedance

The e.m.f. of the glass / reference electrode cell can be measured with a pH meter or other voltmeter with a high input impedance ($>10^{13}$ Ω). If a pH meter with a sensitivity of ± 0.1 mV is used to measure the e.m.f., the sensitivity in determining the pH is ± 0.002 pH units. The use of a $5^{1}/_{2}$ digit voltmeter with a high input impedance (Note 1) can improve the sensitivity to better than $\pm\,0.001$ pH units. (The accuracy of the measurement is dependent upon the reliability of the assignment of pH(S) values to the calibration buffers used.)

4.3 Closed measurement container

It is necessary to measure the pH on a sample that has not had the opportunity to exchange CO_2 with the atmosphere so as to ensure reliable pH results.

4.4 Thermometer (accurate to $\pm$ 0.05 °C)

The temperature should be known or controlled to within 0.1 °C during the measurement.

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[1]   An external circuit based on a high input impedance operational amplifier (*e.g.* an FET electrometer amplifier) configured as a voltage follower (unity gain amplifier) can be used to achieve this.

5. Reagents

5.1 Synthetic seawater

5.1.1 Reagent grade NaCl (dried in an oven at 110 °C)

5.1.2 Reagent grade Na_2SO_4 (dried in an oven at 110 °C)

5.1.3 Reagent grade KCl (dried in an oven at 110 °C)

5.1.4 Calibrated solution of reagent grade $MgCl_2$ (Note 2)

5.1.5 Calibrated solution of reagent grade $CaCl_2$ (Note 2)

5.1.6 Deionized water

5.2 Buffer substances

5.2.1 Calibrated solution of HCl prepared from redistilled reagent grade HCl. Its concentration should be known to within 0.1% (Note 3).

5.2.2 2-amino-2-hydroxymethyl-1,3-propanediol ("tris"), crushed and dried in a desiccator at room temperature over phosphorus (V) oxide before use.

5.2.3 2-aminopyridine, recrystallized from a benzene–petroleum ether mixture, crushed and dried in a desiccator at room temperature over phosphorus (V) oxide before use.

6. Sampling

It is essential that the samples analyzed are collected, poisoned, and stored according to the procedures detailed in SOP 1. Care should be taken to avoid the exchange of CO_2 with the atmosphere both during sampling and during subsequent manipulation.

7. Procedures

7.1 Preparation of buffers in synthetic sea water

The compositions of a tris/HCl buffer and of a 2-aminopyridine/ HCl buffer in a synthetic sea water with a salinity of 35 are given

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[2] Solutions of $MgCl_2$ and $CaCl_2$ can be analyzed either by measuring the density of the stock solution, by titrating with a calibrated silver nitrate solution (*e.g.* using K_2CrO_4 as an indicator) or by gravimetric precipitation of chloride.

[3] Solutions of HCl can be analyzed accurately by coulometric titration, by a careful titration against a standard base (*e.g.* tris—NIST 723)or by gravimetric precipitation of chloride.

in Table 1. This recipe is based on a synthetic sea water (see Chapter 5, Table 6.3) in which 0.04 mol/kg-H_2O of NaCl has been replaced with HCl, and contains a total of 0.08 mol/kg-H_2O of the desired base. The simplest way to prepare this buffer accurately, is first to weigh out the hydrochloric acid and then to scale the amounts of the other constituents to match the exact amount of HCl that was weighed out. Such buffers can be stored for a few weeks, in a sealed, almost full, container.

Table 1: Composition of a buffer solution for pH in a synthetic sea water of salinity 35 (weights based on 1000 g of H_2O).

Constituent	Moles	Weight (g)[a]
NaCl	0.38762[b]	22.6446
KCl	0.01058	0.7884
$MgCl_2$	0.05474	—
$CaCl_2$	0.01075	—
Na_2SO_4	0.02927	4.1563
HCl	0.04000	—
One of:		
2-amino-2-hydroxymethyl-1,3-propanediol (tris)	0.08000	9.6837
2-aminopyridine	0.08000	7.5231
Total weight of solution containing:		
2-amino-2-hydroxymethyl-1,3-propanediol (tris)		1044.09
2-aminopyridine		1041.93

a. Weight in air at sea level (*i.e.* not corrected to mass). If a weight is not given, the component is added as the appropriate amount of a calibrated solution.
b. $m(NaCl) = 0.42762 - 0.04$ mol/kg-H_2O, *i.e.* replacing NaCl with HCl.

To compute the composition for a buffer with a salinity different to 35 (Note 4), first compute the composition of the basic artificial sea water—containing no base or HCl and with the full amount of NaCl—corresponding to the new salinity, S:

$$m_S = m_{35} \times \frac{25.5695S}{1000 - 1.0019S} \ , \tag{4}$$

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4   The magnitude of the error involved in using a salinity 35 buffer for most oceanic measurements (*i.e.* in the salinity range 33–37) is probably less than 0.005 in pH. For a more complete discussion of this error see Whitfield *et al.* (1985) and Butler *et al.* (1985).

then adjust the m(NaCl) down by 0.04 mol/kg-H_2O and add 0.08 mol/kg-H_2O of base.

7.2   *Confirm response of pH cell (Note 5)*

Before a pH cell (a glass electrode / reference electrode pair) is used to measure pH, it should be tested to ensure that it is performing properly, *i.e.* that it has an ideal Nernst response.

Bring both buffers (tris and 2-aminopyridine) to the same, known temperature (*e.g.* 25 °C). Measure and record the e.m.f. of the pH cell in each buffer. The difference in the e.m.f.s is used to check the response of the pH cell (§ 8.1). If the response is not theoretical (within the experimental uncertainty), the electrodes should be rejected. E.m.f. readings obtained with a well-behaved pH cell should be stable with time (drift < 0.05 mV·min^{-1}).

7.3   *Measurement of pH*

Bring the tris buffer and the sea water samples to be measured to the same, known temperature (*e.g.* 25 °C). The e.m.f. of the pH cell is then measured, first in the tris buffer (E_S) and then in the sea water sample (E_X). Care should be taken to minimize any exposure of the sea water samples to the atmosphere so as to limit loss or gain of CO_2.

8.   Calculation and expression of results

8.1   *Calculation of response of pH cell*

The defined pH values of the two buffers recommended for use in this procedure are:

2-amino-2-hydroxy-1,3-propanediol (tris)

$$\mathrm{pH(S)} = \frac{11997.0 + 3.7669S + 0.00178S^2}{T/K} - 381.3088 - 0.011634S$$
$$+ 67.63163 \ \ln(T/K) - 0.121538(T/K) - \log(1 - 0.00106S) \ \ . \tag{5}$$

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[5]   Some investigators make use of the titration curve obtained from titrating a sodium chloride solution with HCl (see SOP 3) to confirm that the electrode pair has the theoretical response *(RT/F)*. However, the value of the slope and the value of $E°$ obtained by fitting experimental results in this fashion are highly correlated and thus not particularly reliable. It is better to verify the response of the electrode pair used with suitable buffers as is done here.

2-aminopyridine (AMP)

$$\mathrm{pH(S)} = \frac{111.35 + 5.44875S}{T/K} + 41.6775 - 0.015683S$$

$$- 6.20815 \ln(T/K) - \log(1 - 0.00106S) \ . \qquad (6)$$

The electrode response (s) can then be calculated:

$$s = \frac{E_{AMP} - E_{TRIS}}{\mathrm{pH(S)}_{TRIS} - \mathrm{pH(S)}_{AMP}} \ , \qquad (7)$$

and compared with the ideal Nernst value: $RT \ln 10 / F$. If it is more than about 0.3% different the pH cell should be replaced.

8.2 Calculation of pH

Values of pH are calculated from the expression

$$\mathrm{pH}(X) = \mathrm{pH(S)} + \frac{E_S - E_X}{RT\ln 10/F} \ . \qquad (8)$$

where pH(S), the pH of tris buffer (Table 1) on the total hydrogen ion scale (expressed in mol/kg-soln) is given by Equation (5).

8.3 Example calculations

Input data:

$$
\begin{aligned}
t &= 25 \ ^{\circ}\mathrm{C} \ (\textit{i.e.} \ T = 298.15 \ \mathrm{K}) \ , \\
S &= 35 \ , \\
E_{TRIS} &= -0.0720 \ \mathrm{V} \ , \\
E_{AMP} &= \ \ \ 0.0049 \ \mathrm{V} \ , \\
E_X &= -0.0670 \ \mathrm{V} \ .
\end{aligned}
$$

Hence

$$
\begin{aligned}
\mathrm{pH(S)}_{TRIS} &= 8.089_3; \\
\mathrm{pH(S)}_{AMP} &= 6.786_6; \\
RT \ln 10 / F &= 0.05916 \ \mathrm{V} / \mathrm{pH \ unit} \ .
\end{aligned}
$$

Thus

$$s = \frac{0.0049 - (-0.0720)}{8.0893 - 6.7866} = 0.05903 \ \ \mathrm{V} / \mathrm{pH \ unit} \ ;$$

and

$$\mathrm{pH}(X) = 8.0893 + \frac{-0.0720 - (-0.0670)}{0.05916} = 8.0048 \ \ .$$

9.   Quality assurance

9.1   For general principles of analytical quality control see Chapter 3.

9.2   Specific applications of analytical quality control

9.2.1   Ideality of pH cell behavior

The measured electrode response (s) should be compared with ideal Nernst behavior on a regular basis (see § 7.2). If the value is more than 0.3% from theoretical, try cleaning the glass electrode of surface deposits and measuring again. If the discrepancy persists, the electrode should be replaced.

The value of E_S in tris buffer when measured at a constant temperature (*e.g.* 25 °C) should remain stable to within a few mV. A sudden change in E_S is indicative of potential problems. Similarly, the e.m.f. of a well-behaved pH cell immersed in a thermostated buffer should be stable (drift < 0.05 mV / min).

9.2.2   Precision

A precision of 0.003 pH units (1 std. dev.) is possible with care. Plot the results of duplicate analyses on a range control chart (SOP 22).

9.2.3   Bias

The bias of potentiometric pH measurements depends on the care with which the buffer was prepared, especially with regard to the ratio between the tris and the HCl, and on the accuracy with which the values of pH(S) were originally assigned. This latter value has been estimated as being within 0.004 pH units.

References

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