

PRACTICAL pH MEASUREMENTS ON NATURAL WATERS

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(1) Dilute solutions and freshwater including 'acid-rain' samples ($I < 0.02 \text{ mol kg}^{-1}$)

Major problems could be encountered due to errors associated with the liquid junction. It is recommended that either a free diffusion junction is used or it is verified that the junction is working correctly using dilute solutions as follows. For commercial electrodes calibrated with IUPAC aqueous RVS or PS standards, the $\text{pH}(X)$ of dilute solutions should be within ± 0.02 of those given in Table 1. The difference in determined $\text{pH}(X)$ between a stirred and unstirred dilute solution should be < 0.02 . The characteristics of glass electrodes are such that below pH 5 the readings should be stable within 2 min, but for pH 5 to 8.8 or so minutes may be necessary to attain stability. Interpretation of $\text{pH}(X)$ measured in this way in terms of activity of hydrogen ion, a_{H^+} , is subject¹ to an uncertainty of ± 0.02 in pH.

(2) Seawater

Measurements made by calibration of electrodes with IUPAC aqueous RVS or PS standards to obtain $\text{pH}(X)$ are perfectly valid. However, the interpretation of $\text{pH}(X)$ in terms of the activity of hydrogen ion is complicated by the non zero residual liquid junction potential as well as by systematic differences between electrode pairs, principally attributable to the reference electrode. For 35‰ salinity seawater ($S = 0.035$) a_{H^+} calculated from $\text{pH}(X)$ is typically 12% too low. Special seawater pH scales have been devised to overcome this problem:

(i) The total hydrogen ion scale, pH_T , is defined in terms of the sum of free and complexed (total) hydrogen ion concentrations, where

$${}^T C_{\text{H}} = [\text{H}^+] + [\text{HSO}_4^-] + [\text{HF}].$$

$$\text{So, } \text{pH}_T = -\log {}^T C_{\text{H}}$$

Calibration of the electrodes with a buffer having a composition similar to that of seawater, to which pH_T has been assigned, results in values of $\text{pHT}(X)$ (Tables 2, 3) which are accurately interpretable in terms of ${}^T C_{\text{H}}$.

(ii) The free hydrogen ion scale, pH_F , is defined, and fully interpretable, in terms of the concentration of free hydrogen ions.

$$\text{pH}_F = -\log [\text{H}^+]$$

Values of pH_F as a function of temperature have been assigned to the same set of pH_T seawater buffers, and so alternatively can be used for calibration (Tables 2, 3)^{2,3}

(3) Estuarine water

Prescriptions for seawater scale buffers are available for a range of salinities. Reliable estuarine pH measurements can be made by calibrating with a buffer of the same salinity as the sample. However, these buffers are difficult to prepare and their use presumes prior knowledge of salinity of the sample. Interpretable measurements of estuarine pH can be made by calibration with IUPAC aqueous RVS or PS standards if the electrode pair is additionally calibrated using a 20‰ salinity seawater buffer.⁴ The difference between the assigned pH_{sws} of the seawater buffer and its measured $\text{pH}(X)$ value using RVS or PS standards is

$$\Delta\text{pH} = \text{pH}_{\text{sws}} - \text{pH}(X)$$

Values of ΔpH should be in the range of 0.08 to 0.18. It empirically corrects for differences between the two pH scales and for measurement errors associated with the electrode pair. The $\text{pH}(X)$ of samples measured using IUPAC aqueous buffers, can be converted to pH_T or pH_F using the appropriate measured ΔpH :

$$\text{pH}_T = \text{pH}(X) - \Delta\text{pH}$$

$$\text{or } \text{pH}_F = \text{pH}(X) - \Delta\text{pH}$$

This simple procedure is appropriate to pH measurement at salinities from 2‰ to 35‰. For salinities lower than 2‰ the procedures for freshwaters should be adopted.

References

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TABLE 1. pH of Dilute Solutions at 25°C, Degassed and Equilibrated with Air, Suitable as Quality Control Standards

	Ionic strength	Concentration(x)	pH	pH
	mmol kg ⁻¹	mmol kg ⁻¹	$p_{\text{CO}_2} = 0$	$p_{\text{CO}_2} = \text{air}$
Potassium hydrogen phthalate	10.7	10	4.12	4.12
	1.1	1	4.33	4.33
$x\text{KH}_2\text{PO}_4 + x\text{Na}_2\text{HPO}_4$	9.9	2.5	7.07	7.05
$x\text{KH}_2\text{PO}_4 + 3.5x\text{Na}_2\text{HPO}_4$	10	0.87	7.61	7.58
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	10	5	9.20	—
HCl	0.1	0.1	4.03	4.03
SRM2694-I ^a	—	—	4.30	—
SRM2694-II ^a	—	—	3.59	—

Note: The pH of solutions near to pH 4 is virtually independent of temperature over the range of 5 to 30°C.

^a Simulated rainwater samples are available (Reference 5) from NIST containing sulfate, nitrate, chloride, fluoride, sodium, potassium, calcium and magnesium.

TABLE 2. Composition of Seawater Buffer of Salinity S = 35‰ at 25°C (Reference 3)

Solute	mol dm ⁻³	mol kg ⁻¹	g kg ⁻¹	g dm ⁻³
NaCl	0.3666	0.3493	20.416	20.946
Na_2SO_4	0.02926	0.02788	3.96	4.063
KCl	0.01058	0.01008	0.752	0.772
CaCl_2	0.01077	0.01026	1.139	1.169
MgCl_2	0.05518	0.05258	5.006	5.139
Tris	0.06	0.05717	6.926	7.106
Tris · HCl	0.06	0.05717	9.010	9.244

Tris = tris(hydroxymethyl)aminomethane ($\text{HOCH}_2)_3\text{CNH}_2$.

A 20‰ buffer is made by diluting the 35‰ in the ratio 20:35.

TABLE 3. Assigned Values of 20‰ and 35‰ Buffers on Free and Total Hydrogen Ion Scales. Calculated from Equations Provided by Millero (Reference 3)

Temp (°C)	pH_T	pH_T	pH_F	pH_F
	S = 20‰	S = 35‰	S = 20‰	S = 35‰
5	8.683	8.718	8.759	8.81
10	8.513	8.542	8.597	8.647
15	8.351	8.374	8.442	8.491
20	8.195	8.212	8.292	8.341
25	8.045	8.057	8.149	8.197
30	7.901	7.908	8.011	8.059
35	7.762	7.764	7.879	7.926