Determination pH of seawater

By Dr. Somkiat Khokiattiwong
Phuket Marine Biological Center, Phuket 83000, Thailand

Determination of the pH of sea water using the indicator dye \textit{m}-cresol purple

\[ \text{pH} = pK(\text{HI}^-) + \log_{10} \frac{[\text{I}^2^-]}{[\text{HI}^-]} \]

\[ \frac{[\text{I}^2^-]}{[\text{HI}^-]} = \frac{A_1/A_2 - \frac{\varepsilon_1(\text{HI}^-)}{\varepsilon_2(\text{HI}^-)}}{\varepsilon_1(\text{I}^2^-)/\varepsilon_2(\text{HI}^-) - (A_1/A_2)\varepsilon_2(\text{I}^2^-)/\varepsilon_2(\text{HI}^-)} \]

\[ \text{pH} = pK_2^+ + \log_{10} \frac{A_1/A_2 - \frac{\varepsilon_1(\text{HI}^-)}{\varepsilon_2(\text{HI}^-)}}{\varepsilon_1(\text{I}^2^-)/\varepsilon_2(\text{HI}^-) - (A_1/A_2)\varepsilon_2(\text{I}^2^-)/\varepsilon_2(\text{HI}^-)} \]

\begin{align*}
\varepsilon_1(\text{HI}^-)/\varepsilon_2(\text{HI}^-) & \quad 0.00691 \\
\varepsilon_1(\text{I}^2^-)/\varepsilon_2(\text{HI}^-) & \quad 2.2220 \\
\varepsilon_2(\text{I}^2^-)/\varepsilon_2(\text{HI}^-) & \quad 0.1331 \\
\end{align*}

\( \lambda_1 = 578 \text{ nm}; \ \lambda_2 = 434 \text{ nm}. \)
Determination of the pH of sea water using the indicator dye *m*-cresol purple

\[
\text{pH} = [\text{pK}_2] + \log_{10} \frac{A_1/A_2 - \varepsilon_1(\text{HI}^-)/\varepsilon_2(\text{HI}^-)}{\varepsilon_1(I^2^-)/\varepsilon_2(\text{HI}^-) - (A_1/A_2)\varepsilon_2(I^2^-)/\varepsilon_2(\text{HI}^-)}
\]

\[
\text{pK}_2 = \frac{1245.69}{(T/K)} + 3.8275 + 0.00211(35 - S)
\]

\( S = \text{Salinity} \)

\( T/K = \text{Temperature (Kelvin: 273.15 K = 0ºC)} \)

where 293 \( \leq T/K \leq 303 \) and 30 \( \leq S \leq 37 \)

**Example:** Salinity = 35, Temperature = 25

\[
\text{pK}_2 = \frac{1245.69}{(273.15+25)} + 3.8275 + 0.00211(35 - 35)
\]

\[
\text{pK}_2 = 8.0056
\]
Determination of the pH of sea water using the indicator dye m-cresol purple

\[
pH = pK_2 + \log_{10} \left( \frac{A_1/A_2 - \varepsilon_1(HI^-)/\varepsilon_2(HI^-)}{\varepsilon_1(I^2^-)/\varepsilon_2(HI^-) - (A_1/A_2)\varepsilon_2(I^2^-)/\varepsilon_2(HI^-)} \right)
\]

\[
A_1/A_2 = \frac{A_{587\,swd} - A_{587\,sw}}{A_{434\,swd} - A_{434\,sw}} - (A_{730\,swd} - A_{730\,sw})
\]

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

\[
(A_1/A_2)_{corr} = (A_1/A_2) - V[0.125 + 0.147(A_1/A_2)]
\]

\[V = \text{volume of m-Cresol Purple added into sample for measurement}\]

\[a \text{ and } b \text{ value for indicator stock solution with } A_1/A_2 = 1.6\]
Determination of the pH of sea water using the indicator dye \( m \)-cresol purple

5. Reagents

5.1 Solution of \( m \)-cresol purple

A concentrated (at least 2 mmol dm\(^{-3}\)) dye solution of known \textit{pH adjusted to be in the range }7.9 \pm 0.1 \textit{pH units}, which is chosen to match pH measurements from an oceanic profile, is required; this implies that for \( m \)-cresol purple \( \frac{A_1}{A_2} \approx 1.6 \).

Note: 1. Solution of \( m \)-Cresol Purple 2 mmole dm\(^{-3}\) was prepared by dissolve 0.202 g of \( m \)-Cresol Purple sodium salt (\( \text{C}_{21}\text{H}_{17}\text{NaO}_5\text{S}; \text{MW}=404.41 \text{ g mol}^{-1} \)) in 250 ml of deionize water. \textit{The pH of the solution will be adjusted with 0.1mol/L of HCl or NaOH to get pH 7.9 \pm 0.1}. 

2. The absorbance ratio (\( A_1/A_2 \)) of a concentrated dye solution can be measured using a cell with a short path length (0.5 mm or less).
6. Sample preparation: filtration for seawater for pH and inorganic carbon analyses

LIMNOLOGY and OCEANOGRAPHY: METHODS

A seawater filtration method suitable for total dissolved inorganic carbon and pH analyses

Emily E. Bockman* and Andrew G. Dickson
Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093

Abstract

High biomass and heavy particle loads may interfere with carbonate chemistry analyses of samples from experimental aquaria and cultures used to investigate the impact of ocean acidification on organisms, as well as from biologically productive coastal regions. For such samples, a filtration method is needed that does not change the dissolved CO₂ content, and consequently does not alter the total dissolved inorganic carbon and pH of the sample. Here, a filtration method is presented in which the sample seawater is pumped by a peristaltic pump through a replaceable 0.45 μm filter in a 50 mm polycarbonate filter holder and then into the sample bottle. Seawater samples of known carbonate composition were filtered to confirm that the filtration method did not alter the CO₂ content, and compromise the subsequent sample analysis and data usefulness. Seawater samples with added phytoplankton concentrations in the range of 1–5 × 10⁶ cells mL⁻¹ were also filtered successfully. Finally, seawater with added biogenic CaCO₃ was tested to prove that the method could successfully filter out such particles and produce dependable results. This approach will help to ensure more consistent and reliable carbonate chemistry measurements in coastal environments and from ocean acidification aquaria and cultures, by providing a well-tested method for sample filtration.
Analysis of pH in Seawater

Sample preparation: filtration for seawater for pH and inorganic carbon analyses
Analysis of pH in Seawater

Sample preparation:
Analysis of pH in Seawater

Sample preparation:

Creating the 1% headspace with the 20 mL syringe
Analysis of pH in Seawater

Sample preparation:

Filling the pipette with saturated mercuric chloride
(about 0.02% of the sample volume)
Analysis of pH in Seawater

Sample preparation:
Determination of the pH of sea water using the indicator dye \textit{m}-cresol purple

7. Procedure

7.1 Warm/Cool temperature of sample cell to 25.0°C (± 0.1°C)
This is done by placing a number of cells in a thermostated compartment (see section 4.6) for a few hours.

7.2 Measure absorbances for the cell + sea water
Clean and dry the exterior of the cell; place the cell in the thermostated sample compartment of the spectrophotometer. Measure and record the absorbances at three wavelengths: a non-absorbing wavelength (730 nm for \textit{m}-cresol purple) and at the wavelengths corresponding to the absorption maxima of the base (I$^2^-$) and acid (HI$^-$) forms of the dye respectively (578 and 434 nm).
Determination of the pH of sea water using the indicator dye m-cresol purple

7. Procedure

7.3 Inject dye into cell
Remove one of the cell caps, add approximately 0.05–0.1 cm$^3$ (depend on the volume of the optical cell) of concentrated dye (~2 mmol dm$^{-3}$) to the sample, replace the cap and gently shake the cell to mix the sea water and dye. The amount of dye required is that which will produce absorbance values of between 0.4 and 1.0 at each of the two absorbance peaks.
Determination of the pH of sea water using the indicator dye \textit{m}-cresol purple

7. Procedure

\textbf{7.4 Measure absorbances of cell + sea water + dye}

Return the cell to the spectrophotometer and again measure the absorbances at the three wavelengths used in section 7.2. Cells should be positioned to maintain consistent alignment(s) between baseline and indicator absorbance measurements.

Note: The difference between the baseline absorbance (sea water only) and the absorbance of the sample + dye at 730 nm should be no greater than $\pm 0.001$ to $\pm 0.003$; if this value is exceeded, the cell should be removed and the optical windows cleaned before the absorbances are measured again.
Determination of the pH of sea water using the indicator dye \(m\)-cresol purple

7. Procedure

8. Calculation and expression of results

Seawater sample: Temp = 25 (control by system), Sal. = 35

\[
pK_2 = \frac{1245.69}{(T/K)} + 3.8275 + 0.00211(35 - S)
\]

\[
pK_2 = \frac{1245.69}{(273.15 + 25)} + 3.8275 + 0.00211(35 - 35)
\]

\[
pK_2 = 8.0056
\]

\[
pH = pK_2 + \log_{10} \frac{A_1/A_2 - \varepsilon_1(HI^-)/\varepsilon_2(HI^-)}{\varepsilon_1(I^2^-)/\varepsilon_2(HI^-) - (A_1/A_2)\varepsilon_2(I^2^-)/\varepsilon_2(HI^-)}
\]
Determination of the pH of sea water using the indicator dye *m*-cresol purple

7. Procedure

8. Calculation and expression of results

*Measured absorbances:*

Sea water (sw): \( A_{434} = 0.02433 ; A_{578} = 0.01936 ; A_{730} = 0.08365 \)

Dye + sea water (swd): \( A_{434} = 0.45123 ; A_{578} = 0.84574 ; A_{730} = 0.08298 \)

\[
\frac{A_1}{A_2} = \frac{\frac{A_{587swd} - A_{587sw}}{A_{434swd} - A_{434sw}}}{\frac{(A_{730swd} - A_{730sw})}{(A_{730swd} - A_{730sw})}}
\]

\[
\frac{A_1}{A_2} = \frac{0.84574 - 0.01936 - (0.08298 - 0.08365)}{0.45123 - 0.02433 - (0.08298 - 0.08365)} = 1.93430
\]

\[
\text{pH} = pK_2 + \log_{10} \left( \frac{A_1/A_2 - \varepsilon_1(\text{HI}^-)/\varepsilon_2(\text{HI}^-)}{\varepsilon_1(\text{I}^2^-)/\varepsilon_2(\text{HI}^-) - (A_1/A_2) \varepsilon_2(\text{I}^2^-)/\varepsilon_2(\text{HI}^-)} \right)
\]
Determination of the pH of sea water using the indicator dye *m*-cresol purple

7. Procedure

8. Calculation and expression of results

\[ \frac{A_1}{A_2} = \frac{A_{587swd} - A_{587sw} - (A_{730swd} - A_{730sw})}{A_{434swd} - A_{434sw} - (A_{730swd} - A_{730sw})} \]

Corrected to zero dye addition \((V = 0.08 \text{ cm}^3)\),

\[ \left( \frac{A_1}{A_2} \right)_{corr} = 1.9343 - 0.08 [0.125 - 0.147(1.93430)] = 1.94705 \]

\[ \text{pH} = pK_2 + \log_{10} \frac{A_1/A_2 - \varepsilon_1(\text{HI}^-)/\varepsilon_2(\text{HI}^-)}{\varepsilon_1(\text{I}^2^-)/\varepsilon_2(\text{HI}^-) - (A_1/A_2) \varepsilon_2(\text{I}^2^-)/\varepsilon_2(\text{HI}^-)} \]
Determination of the pH of sea water using the indicator dye $m$-cresol purple

7. Procedure

8. Calculation and expression of results

\[
pH = 8.0056 + \log_{10} \left( \frac{1.94705 - 0.00691}{2.2220 - 1.94705 \times 0.1331} \right) = 8.0005
\]
Determination of the pH of sea water using the indicator dye \( m \)-cresol purple

**Standard Reference Material:**

SRM: Tris Buffer Solution in synthetic seawater) which provide the high accuracy of pH. (it could be ordered from: co2crms@ucsd.edu)

<table>
<thead>
<tr>
<th></th>
<th>pH Meas.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.0945</td>
</tr>
<tr>
<td>3</td>
<td>8.0960</td>
</tr>
<tr>
<td>4</td>
<td>8.0958</td>
</tr>
<tr>
<td>5</td>
<td>8.0939</td>
</tr>
<tr>
<td>6</td>
<td>8.0956</td>
</tr>
<tr>
<td>7</td>
<td>8.0931</td>
</tr>
<tr>
<td>8</td>
<td>8.0930</td>
</tr>
<tr>
<td>9</td>
<td>8.0942</td>
</tr>
<tr>
<td>10</td>
<td>8.0917</td>
</tr>
<tr>
<td>11</td>
<td>8.0905</td>
</tr>
<tr>
<td>12</td>
<td>Average 8.093818 0.001803</td>
</tr>
</tbody>
</table>