



# Application Bulletin #10

MANTECH INC.  
160 Southgate Drive, Unit 2  
Guelph, Ontario, Canada N1G 4P5  
P: (519) 763-4245  
[www.mantech-inc.com](http://www.mantech-inc.com)

---

## Alkalinity in Seawater

### Introduction:

The total alkalinity of seawater is essentially a measure of the negatively charged ions present in a given sample<sup>1</sup>. In the oceans, the major ions present are bicarbonate and carbonate<sup>1</sup>, however the balance of these ionic species are changing due to increased levels of atmospheric carbon dioxide<sup>2</sup>. Increased dissolved carbon dioxide and bicarbonate concentrations in the ocean (known as ocean carbonation) together with decreased pH and carbonate concentrations (ocean acidification) can have a negative impact on certain marine organisms and ecosystems<sup>2</sup>. Constant monitoring of alkalinity is therefore important for understanding how the world's oceans are dealing with these environmental changes.

In this method, total alkalinity is measured by automated potentiometric titration in an open cell. A seawater sample is first treated with acidic titrant, consisting of hydrochloric acid prepared in a sodium chloride background, to bring the pH down to between 3.5 and 4.0. The sample is then stirred to allow for the escape of any carbon dioxide that has evolved. Subsequently, the titration continues until the sample reaches a pH of 3.0, where one can assume that the total dissolved inorganic carbon and residual bicarbonate ion is approximately zero<sup>3</sup>.

The MANTECH automated system for the titration of alkalinity in seawater samples provides the benefit of automatic pipetting and titration in a water-jacketed vessel for constant temperature control. A nitrogen gas purge valve can be utilized during titration to ensure the sample remains free from any carbon dioxide generated during acid addition. The system also provides intelligent rinsing with the IntelliRinse program which involves continuous flushing of the system until user-specified standards of cleanliness are reached. All results are automatically calculated and reported, including the exporting of data to external locations for further analysis.

From a stand-alone option to fully automated with up to 197 sample positions on the MANTECH AutoMax autosamplers, system operation is simple whether in the laboratory or aboard a ship. Furthermore, the SampleProtect system for automatic covering and uncovering of samples is available to ensure full protection from any additional dissolved carbon dioxide coming from the atmosphere. Please contact your local MANTECH sales representative for more information about how this method can work for you.

**Conforms To:** Carbon Dioxide Information Analysis Center (CDIAC) Guide to Best Practices for Ocean CO<sub>2</sub> Measurements – SOP3b

**Sample:** Seawater samples

**Concentration Range:** This method is applicable for total alkalinities of 2000-2500 umol/kg, typically found in ocean samples. Lower values may be seen in coastal or surface polar waters but may also be analyzed utilizing this method if the volume of the initial acid addition is reduced.

### Apparatus:

1. pH Electrode (PCE-80-PH1013, Thermo ROSS Ultra® pH Electrode, or any other BNC connection electrode)
2. Electrode Cable (PCE-86-EX1001)
3. Interface (PC-1000-102/4)
4. Burivar 1/2 (PC-1104-00)
5. Buret – 5mL (PC-1104-005)
6. TitrasiP (PC-1300-475)

### Reagents:

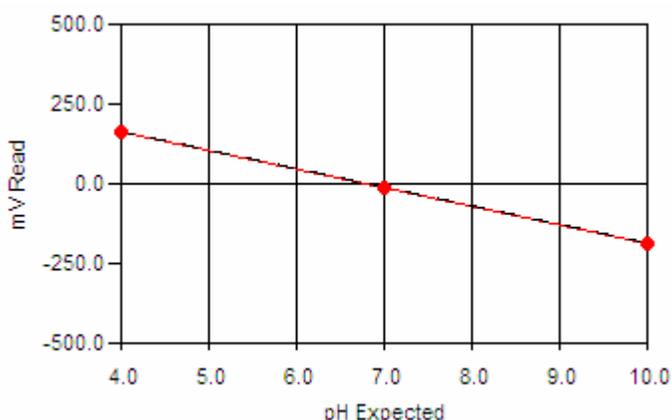
1. Standardized titrant (HCl): 0.1 mol/kg HCl in 0.6 mol/kg NaCl
2. Sodium carbonate solution: 1000 ppm alkalinity = 1.0589 g Na<sub>2</sub>CO<sub>3</sub> in 1L distilled water. Dilute as necessary for other concentrations
3. pH 4, 7, and 10 buffer solutions

### Procedure:

The procedure described below is for a TitrasiP SA system. The system can also be configured to use any MANTECH AutoMax Sampler to automate liquid handling, SampleProtect to allow samples to remain covered until analysis, and a gas purge valve to automate nitrogen purge of the sample.

#### Calibration:

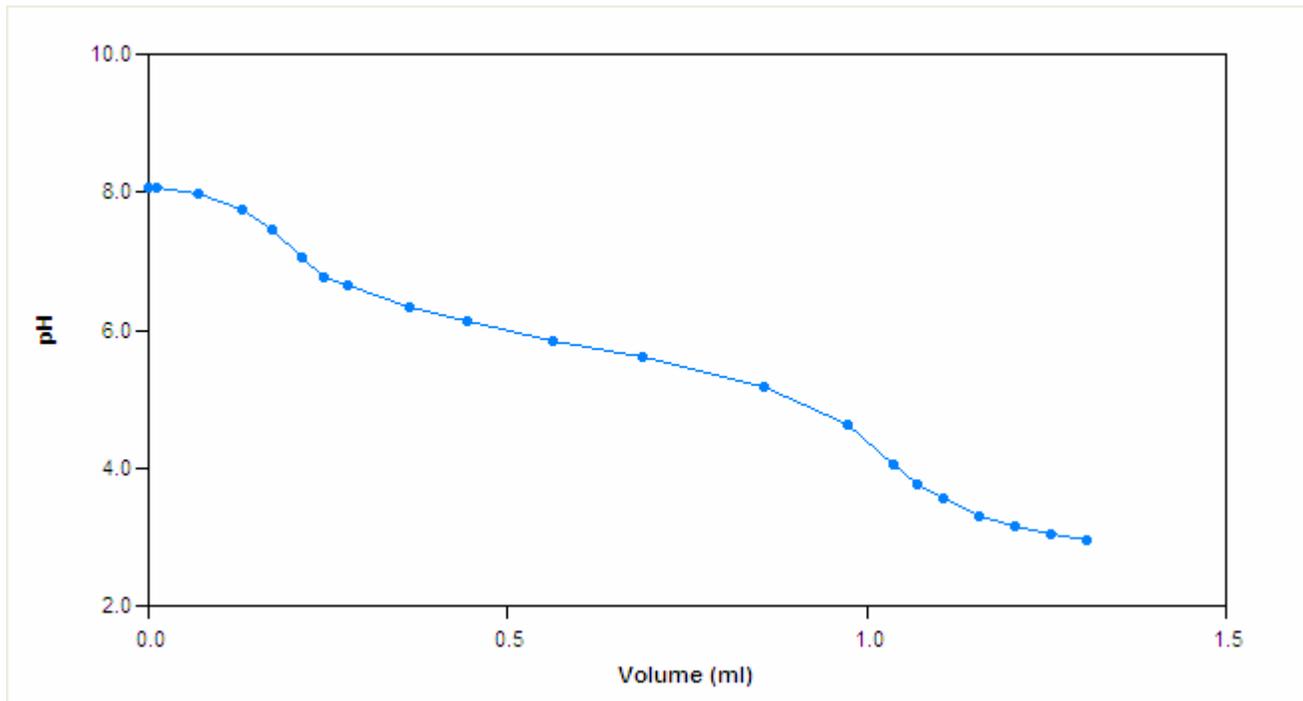
1. The system will ask the user to move the probes to the rinse station where the sample transfer line and TitrasiP vessel are rinsed with deionized water.
2. The system will then ask the user to move the tips to the pH 4 buffer and the sample transfer line will be primed with the pH 4 buffer solution.
3. 25mL of buffer solution will be pumped into the TitrasiP cell and the stirrer will be turned on.
4. The pH of the buffer solution is measured and recorded.
5. Steps 1 to 4 will be repeated for the pH 7 and 10 buffer solutions.
6. The calibration curve will then be calculated and reported



**Figure 1:** Sample Calibration Curve

#### Sample Analysis:

1. The system asks the user to move the probes to the rinse station where the sample transfer line and TitrasiP vessel are rinsed with deionized water.
2. The system then performs a small injection of titrant into the rinse water to ensure the lines are primed with fresh solution. The TitrasiP vessel is then drained and rinsed again with deionised water. The water is checked to ensure the pH of the water in the vessel is between pH 5 and 6 to ensure the cell was sufficiently cleaned following the titrant addition, prior to the next sample being analysed.
3. The system then asks the user to move the probes into the first sample and the transfer line is primed with sample.
4. The specific volume of sample, dependant upon the expected result, 50-125mL, is then pumped into the TitrasiP cell, and the stirrer turned on to 20%.
5. The sample is titrated with standardized titrant to pH 3.7.
6. Stirring is then increased and optional air purge is turned on for 6 minutes to allow excess CO<sub>2</sub> to degas.
7. The sample is then titrated to pH 3 using 0.05mL injections.
8. Volume injected to 0.001mL, e.m.f to 0.01mV, and temperature to 0.01oC is recorded after each injection in the titration. Following completion of the titration, these values are then exported to an external program for further analysis.
9. Steps 1-7 are repeated for each of the remaining samples.



**Figure 2: Sample Titration Curve**

### Hints/Suggestions:

1. Rinse all sample containers with deionized water prior to sample addition to prevent contamination of samplers due to tap water impurities.
2. Avoid the use of soaps or cleaners for washing plastic or glassware. Detergents can contain sodium carbonate which will interfere with alkalinity readings. The use of disposable tubes is recommended.

3. Samples with high alkalinity values should not be left exposed to air for an extended period of time. These samples will slowly decompose, resulting in low alkalinity readings.
4. Ensure that the electrode is completely filled with solution before each run.
5. Electrodes generally last for six months to one year depending on sample type and frequency of use. Samples that are highly acidic, basic, or abrasive will limit the lifespan of the electrode, as will solvent-based samples. It is highly recommended that customers order a new electrode every six months or when the calibration limits have been exceeded.
6. Purge the buret and prime transfer lines daily.
7. Perform a pH calibration (standards: pH 4, 7, 10 buffer solutions) before every run. Calibrations should have a slope of  $59 \pm 4\text{mV/pH}$  unit at  $25^\circ\text{C}$ , and an intercept that is consistent beginning at  $0 \pm 25\text{mV}$  for a new electrode. If the electrode calibration consistently falls outside these limits, the electrode has been worn out or over-aged and erratic pH readings may result. The electrode should be discarded and a new electrode should be used.
8. pH measurements are usually combined with an alkalinity titration. PH is measured prior to the addition of titrant.

---

<sup>1</sup> *Sea Water CO<sub>2</sub>*. Retrieved September 13, 2010, from the Scripps Institution of Oceanography website:  
[http://scrippsco2.ucsd.edu/research/sea\\_water\\_co2\\_3.html](http://scrippsco2.ucsd.edu/research/sea_water_co2_3.html)

<sup>2</sup> Schultz, K.G., Barcelos e Ramos, J., Zeebe, R.E., Riebesell, U. (2009). CO<sub>2</sub> perturbation experiments: similarities and differences between dissolved inorganic carbon and total alkalinity manipulations. *Biogeosciences*, 6, 2145-53.

<sup>3</sup> Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. *Guide to best practices for ocean CO<sub>2</sub> measurements*. PICES Special Publication 3, 191 pp.