

## The Determination of Carbon Dioxide System Parameters in Aquatic Systems

Carbon dioxide is the dominant end product of organic carbon degradation in almost all aquatic environments and its variation is often a measure of net ecosystem metabolism<sup>[1-3]</sup>. Therefore, in aquatic biogeochemical studies, it is desirable to measure parameters that define the carbon dioxide system. CO<sub>2</sub> is also the most important green house gas on Earth. Its fluxes across the air-water or sediment-water interface are among the most important concerns in global change studies and are often a measure of the net ecosystem production/metabolism of the aquatic system.

There are four readily measurable parameters of the aquatic carbon dioxide system: pH, *p*CO<sub>2</sub>, total dissolved inorganic carbon (DIC) and total alkalinity (TA).

Surface water *p*CO<sub>2</sub> can be measured by an underway CO<sub>2</sub> equilibration chamber and an infrared CO<sub>2</sub> analyzer, such as the Apollo SciTech's AS-*p*CO<sub>2</sub>-1, or by photometric methods<sup>[5, 6]</sup>. In the formal method, CO<sub>2</sub> equilibrated air is sent into the Li-Cor CO<sub>2</sub> analyzer for quantification against a standard gas. The Apollo SciTech will develop your underway (i.e., real-time) surface water *p*CO<sub>2</sub> analyzer using any Li-Cor analyzer (LI6262 or LI7000) and a personal GPS to suit your needs.

The CO<sub>2</sub> flux across the air-sea interface is calculated by the following widely used one-dimensional stagnant thin-film model<sup>[7]</sup>:

$$\text{CO}_2 \text{ Flux} = k\beta(p\text{CO}_{2w} - p\text{CO}_{2a}).$$

where *k* is the gas transfer velocity;  $\beta$  (Bunsen coefficient) is the solubility of CO<sub>2</sub> at given temperature and salinity<sup>[8]</sup>. *p*CO<sub>2w</sub> and *p*CO<sub>2a</sub> represent the partial pressure of CO<sub>2</sub> in surface water and overlaying air, respectively. Most of uncertainty in this calculation results from estimation of gas transfer velocity (*k*), which is empirically derived from sea surface wind speed. Two sets of most frequently used “*k* vs. wind speed” relationships are those of Wanninkhof<sup>[9]</sup> and Liss and Merlivat<sup>[10]</sup>.

DIC is the total dissolved inorganic carbon and is defined as:

$$\text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

Where  $[\text{CO}_2^*] = [\text{CO}_{2aq}] + [\text{H}_2\text{CO}_3]$ . Aquatic scientists measure DIC most often by acidification of water samples and subsequent quantification of the extracted CO<sub>2</sub> gas by a Coulometer or by an infrared CO<sub>2</sub> analyzer<sup>[11]</sup>. DIC can be measured very precisely (0.05-0.1%) and accurately (0.1-0.2%) using a coulometer when sample volume is not limiting (more than 10 mL) and Certified

Standard Reference Materials (CRMs) are used for calibration purposes. The Apollo SciTech's AC-C2 DIC analyzer uses a Li-Cor 6262 CO<sub>2</sub> analyzer and achieves a precision of 0.1% or better in laboratory conditions using only 0.5 mL of water sample (see products for more information). A great advantage of this method is that within 1-2 minutes, 100% of CO<sub>2</sub> is extracted from the water. Thus samples with a wide range of DIC values (i.e., sediment porewaters) can be measured precisely. Also because of small sample volume, time series analysis can be performed on volume-limited systems (i.e., measuring respiration in culture or incubation).

TA is the deficiency of H<sup>+</sup> or the excess base with respect to the zero proton level at the CO<sub>2</sub> equivalence point (about pH = 4.5) <sup>[12, 13]</sup>. Alkalinity by this definition can be determined by HCl titration of the water sample to the CO<sub>2</sub> equivalence point (the Gran titration <sup>[14]</sup>) or by a curve fitting method. Mathematically, it is defined as

$$\text{TA} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{B}(\text{OH})_4^-] + 2[\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] - [\text{H}_3\text{PO}_4] + [\text{SiO}(\text{OH})_3^-] + \dots \text{contributions of other minor acid or base species} \quad (9)$$

With water sample volumes greater than 20 mL, TA in seawater can be measured to a precision of 0.1% or better. Certified Standard Reference Materials for alkalinity have been in use since 1996 <sup>[15]</sup>. With these standards, the reported accuracy of analyses is better than ±0.2 % <sup>[11, 15, 16]</sup>. The Apollo SciTech's AC-A2 Alkalinity Titrator provides automated Gran titration and result calculation. It achieves a precision of 0.1% or better in laboratory conditions (see products for more information).

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