

# A Comparison of methods for measuring Dissolved CO2

*Chemical Analysis against the OxyGuard CO2*

## **Two methods for Chemical Analysis**

The two common chemical analysis methods for the determination of dissolved CO<sub>2</sub> were originally designed for steam boiler feed water, which is very pure. Aquaculture water, seawater, tapwater and water from lakes, ponds, rivers, wells etc all contain substances that interfere with a chemical analysis. Results obtained using chemical analysis on aquaculture water are therefore always too high. There are also technical problems involved that can introduce errors.

The two commonly used methods are both based on titration. A certain volume of the water to be analysed is taken, and base or acid is added until either pH 8.2 or pH 4.3 is reached. The amount of acid or base added is measured and a calculation made to determine the CO<sub>2</sub> content of the water.

### **The 8.2 method is the easiest to understand:**

By adding hydroxide to water containing CO<sub>2</sub> the following chemical reaction takes place:



At pH 8.2 all of the CO<sub>2</sub> has been converted to HCO<sub>3</sub><sup>-</sup>. By measuring how much hydroxide was added to the sample of known volume the CO<sub>2</sub> content can be calculated. There are several test kits available for this method. Typically two drops of colour pH indicator are added to a 50 ml sample in a beaker. Sodium hydroxide is added using a small syringe until the sample changes colour. The amount of sodium hydroxide added is determined by looking at the syringe, and a quick calculation gives the result. When used on aquaculture water the following errors are likely:

It is very difficult in the field to take a small size sample of exact volume. A typical variation is +/- 1 ml. Relative to 50 ml., this is an error of +/-2%.

The titration end-point 8.2 is only valid at 25 degrees Celsius. At other temperatures the end-point is different. Aquaculture water does not often have a temperature of 25 degrees Celsius!

It can be very difficult to observe exactly when a pH indicator changes to a certain colour. It is even more difficult in turbid or slightly coloured water. This can be overcome by using a pH meter, but the practical accuracy of a pH meter is also limited - more about this later.

Ammonium is one of the more significant dissolved substances (other than CO<sub>2</sub>) in aquaculture water that reacts with sodium hydroxide. 1 mg/l of ammonium (NH<sub>4</sub><sup>+</sup>) consumes base as approximately 0.2 mg/l of CO<sub>2</sub>. So if you have 50 mg/l of ammonium then your CO<sub>2</sub> determination will be 10 mg/l too high.

Phosphates, such as H<sub>2</sub>PO<sub>4</sub><sup>-</sup> interfere too, and even more strongly than ammonium: 1 mg/l of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> corresponds to almost 0.5 mg/l of CO<sub>2</sub>!

Ammonium and phosphates are, of course, inevitable by-products formed when fish digest the feed they are given, and these are just two of the substances that can interfere.

### **The 4.3 method is a little more complex:**

This method uses the fact that the ratio of CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> in a sample depends on the pH. The ratio is found by accurately measuring the pH. Then a titration with acid is performed to pH 4.3 to convert all the H<sub>2</sub>CO<sub>3</sub><sup>-</sup> to CO<sub>2</sub>. This gives a measurement of how much H<sub>2</sub>CO<sub>3</sub><sup>-</sup> there was and from this and the ratio the CO<sub>2</sub> content of the sample can be determined.

This method also only works at 25 degrees Celsius, and has the same problems of taking a precise small size sample as described above. In addition to this the pH measurement has to be very precise. In practice the accuracy of a pH measurement is probably +/- 0.2 pH - (although most pH meters display values with 2 decimals!) This uncertainty affects the CO<sub>2</sub> determination by some +/- 10%.

This method also suffers from chemical interference. Ammonium does not interfere here, but phosphates certainly do, as well as anything else that reacts with acid. Depending on the actual water quality the error is variable, but it is always positive, thus again leading to too high CO<sub>2</sub> numbers.

The complete list of whatever interferes with either method is very long. Anything that reacts with either base, acid or both will interfere. For example ammonium, phosphates, silicates, borates, nitrites, humic acids, fat, amino acids, urea, dissolved iron and many more.

### **The OxyGuard CO<sub>2</sub> measures directly - and accurately**

The OxyGuard CO<sub>2</sub> Analyzer does not use any chemistry, but measures the CO<sub>2</sub> gas that is dissolved in the water. Its measuring principle is based on selective partial pressure measurement. It responds only to CO<sub>2</sub> gas, and is completely insensitive to any other gas that can be dissolved in water, such as oxygen, nitrogen, argon, etc. It therefore gives a reliable, accurate result.

It is OxyGuard's hope that this instrument will help the aquaculture industry make further progress into facilitating the intensive production of high-quality fish under the best possible conditions.