

Carbon Dioxide Tests For The Marine Aquarium

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By Craig Bingman

Several times over the last several months, a newcomer to the reef aquarium hobby has asked the Internet Reef newsgroups whether or not he or she should obtain a carbon dioxide test kit for their new aquarium. Such test kits are often bundled with "limnology" or "master" test kit collections.

There are also a few recommendations in the popular aquarium literature about what the correct carbon dioxide level for a marine aquarium should be. So, confusion about this issue is quite understandable. One could easily develop the impression that a carbon dioxide test kit would be a valuable addition.

Unfortunately, the answer is "no, carbon dioxide test kit is not necessary nor is it recommended for use in marine aquaria." This month I will briefly describe why this is the case.

It helps to understand how carbon dioxide test kits work and what they are actually measuring. Although they are called "carbon dioxide" kits, a more realistic description of them would be specialized "acidity" test kits. Acidity is the inverse of alkalinity, a term that will be more familiar to marine hobbyists. Whereas alkalinity is a measurement of the capacity of a water sample to resist downward pH change upon addition of acid, an acidity test kit measures the capacity of a water sample to resist upward pH change when titrated with an alkaline reagent.

There isn't anything special about the reagents used in these test kits...they aren't magical and don't respond only to carbon dioxide. They will respond to many acids that might be present in the sample. Whatever selectivity exists in these test kits is provided only by the choice of titration endpoint, the final pH value where the color of the indicator changes and the titration is considered to be complete. The endpoint indicator for commercial carbon dioxide test kits is almost invariably phenolphthalein, which has a color endpoint at pH 8.3.

At this point you will begin to see why these test kits are not especially useful for reef aquarists. A pH value of 8.3 is typical for many reef systems. So, when you add the color indicator to the water sample, it immediately gives the endpoint color. So, you realize that either the test kit isn't working correctly or you have wasted your money. In this case, both are true.

The carbon dioxide test kits on the market are all calibrated to work correctly for freshwater samples. There are some assumptions about the thermodynamic properties of the carbon dioxide system in the water sample built into the test kit. For commercial carbon dioxide kits, those assumptions are approximately valid for freshwater samples, but are completely invalid for marine samples.

The biggest flaw arises from the fact that the pKa value for bicarbonate/carbonate equilibrium is shifted downward by over a pH unit in marine samples. The test kit proposes to measure carbon dioxide by a simple addition of alkaline reagent to the sample. In a typical freshwater sample, the addition of that alkaline reagent would be almost exclusively converting carbon dioxide to bicarbonate ions. Because of the downward shift in the carbonate pKa in seawater, under most circumstances, the aquarist will mainly be titrating bicarbonate ions to carbonate ions. So, carbon dioxide test kits read artificially high with seawater samples.

So, does this mean it is impossible for an aquarist to determine the carbon dioxide concentration in a reef aquarium? No. But my first question would be why are you trying to measure carbon dioxide in your reef aquarium in the first place? If the answer is because you have read a recommendation for carbon dioxide in reef tanks from the popular aquarium literature (less than 2.0 milligrams per liter in the *Natural Reef Aquariums* by John Tullock), then you really are looking to the wrong sources for information about aquarium chemistry.

The amount of carbon dioxide in a marine sample can be uniquely determined by accurate pH and total alkalinity measurements (see the "Biochemistry of Aquaria" column in the January 1998 issue of *Aquarium Frontiers* located in the "Archive" section of this web site, for a look at the "Calculation of Calcium Carbonate Saturation States in Reef Aquaria"). You probably already have some way of measuring pH and total alkalinity. If you don't, you probably should get equipment for measuring these two parameters because they are quite important in reef aquarium husbandry. Moreover, I would tend to challenge the idea that the carbon dioxide concentration ever becomes problematically high in a home reef aquarium. If

it does, then very likely the system has much more serious problems like very low dissolved oxygen concentration.

So, there is absolutely no reason for marine aquarists to buy a carbon dioxide test kit for testing aquarium water if they have a pH monitor and a good total alkalinity test kit. The money you might spend on a carbon dioxide test kit would be more productively invested in a dissolved oxygen titration test kit.

Are carbon dioxide test kits ever useful for the home aquarist? What about freshwater planted tanks? Well, there are carbon dioxide/pH/total alkalinity tables available for freshwater aquarists (for example, on the Dupla web site) and they work reasonably well, provided the total alkalinity in the aquarium is coming mainly from bicarbonate ions. If other unknown buffering substances are present, then the tables will fail to give valid answers.

Unfortunately, the titration test kits for carbon dioxide will also fail under conditions when significant concentrations of other buffering substances are present. So, you really haven't gained anything at all by obtaining a carbon dioxide test kit. You have simply exchanged one invalid test methodology for another.

What would interfere with these test methods in freshwater tanks? Literally any (non-bicarbonate or carbonate) buffer substance that might be added will absolutely confound both these test methods. Of course, one wonders why these additional buffer substances would be added to a freshwater planted tank if carbon dioxide injection is being used. You should be able to set the pH of the aquarium wherever you wish by simply feathering the rate of carbon dioxide injection into the tank and by appropriate adjustment of bicarbonate alkalinity.

Marine buffers present the same problem for accurate measurements of alkalinity in marine systems. More precisely, when buffer substances like borate are used, the assumption that the carbonate alkalinity is approximately equal to the total alkalinity goes out the window. These buffers will also destroy any validity of carbon dioxide test kits, because boric acid will interfere with the carbon dioxide test kit in marine samples. Again, save your money and avoid carbon dioxide test kits.