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The Temporary Hardness of Aquarium Water

Alkalinity -
Among aquarists there seems to be some confusion about the Hardness of the aquarium water. Most aquarists only consider one sort of hardness, the so-called "soap hardness" or "total hardness" that may be found when shaking for example 40 ccm of water with some soap solution (Boutron-Boudet) or 100 ccm with a more diluted soap solution (Clark). This hardness might also be found using the Komplexon etc. In my aquarium-keeping, I never found this sort of hardness to be of prior importance.

There is another sort of hardness, called Temporary Hardness or, better, Carbonate Hardness that seems to be of much greater importance when keeping fish which are said to like "soft water". By the analysis of soap hardness one finds the amount of bicarbonate/carbonate ions present in the water. That is to say that these two analyses give information about two different matters within the composition of the water. You possibly know that the amount of salts from carbonic acid (carbonates and bicarbonates, also called hydrocarbonates) present in the water normally governs the pH value of the water. This is done by the so-called hydrolysis of salts of carbonic acid. $CaCO_3$ or calcium carbonate will split into ions if dissolved in water. $CaCO_3 = Ca^{2+}$ plus CO_3^{--} that is to say into one Ca^{2+} ion with 2 positive electrical charges and one carbonate ion with 2 negative charges. The carbonate ion however is able to stay in water in that form. It acts with water (the hydrogen ions of the water) in this way:

CO_3^{--} plus $H_2O = HCO_3^-$ plus OH^-.

That is to say that the carbonate ion "steals" a hydrogen ion and in that way one hydroxyl ion is left in the water. This makes water alkaline or, in other words, the pH of the water increases. The carbonate ion is converted into a bicarbonate ion. This however cannot stay in water in that form, it has to undergo one more metamorphosis:

HCO_3^- plus $H_2O = H_2CO_3$ plus OH^-

The bicarbonate ion steals another hydrogen ion from the water and converts itself into common carbonic acid. One hydroxyl ion is left in the water, making this even more alkaline.

These reactions take place because carbonic acid is a weak acid. A weak acid will not freely split itself into ions when dissolved into water. Only very few of the acid molecules will separate into ions. Therefore carbonate and bicarbonate ions (independently where they come from) will have to establish the natural balance between complete acid molecules, carbonate, and bicarbonate ions. The presence of calcium ions has nothing to do with this reaction. It is only a question of how much carbonate you add to the water. The more carbonate added, the more the pH of the water will increase!!! The presence of carbon dioxide in water (carbon dioxide, not supplies to the water from salts of carbonic acid) acts as if carbonic acid is present and thereby forces the balance into a less alkaline water or a lower pH value. Ion exhange materials (permutit, natrolit, etc.) that decrease the soap hardness to zero will not interfere with the balance between carbonic acid and its salts. The pH of the water (generally) will not change. Using these common "water improvers" only changes "lime" into "soda".

The analysis:

Take 100 ccm (1/10 liter) of the water to be analyzed. Place this amount of water into a white cup (clean) or a cylindric glass placed on a white support. Add as many drops of 0.1% methyl orange (or perhaps even better the "screened MO indicator" (The British Drug House Ltd. CN 2075.B.D.H. "3046" indicator)) as you clearly see the orange yellow coloring of the water. Fill your "hardness burette" (or other test tube) with 0.1 normal hydrochloric acid (0.1 n HCl), a titration acid to be bought at your drug house. Add this acid to the water sample drop by drop. Stir the sample gently. When the color changes from orange yellow to orange red the analysis is over. If you used the common test tube for "soap hardness", one degree of hardness read on the tube equals 1/10 ccm. As one degree of alkalinity (SBV-Wert) is 1 ccm 0.1 n HCl per 100 ccm water sample, you just read the degree of "hardness" on your test tube and divide it by 10.

Let us say that you used an amount of acid equal to 12 "degrees of hardness", measured on the test tube, your Alk value is 1.2 (you used 1.2 ccm of acid). The temporary hardness you now find my multiplying this value by 2.8: 2.8 x 1.2 = 3.6 German degrees of temporary hardness (see also pages before).

Theory of the analysis:

Hydrochloric acid is a very strong acid. If added to a water sample that holds salts of carbonic acid, the hydrochloric acid will "force" the salts into chlorides (force the bicarbonate and carbonate into carbonic acid). The carbonic acid however is not able to decrease the pH value of the water down to the value by which the methylorange changes its color (about pH 3.6). Therefore, the methylorange does not change its color before there is free hydrochloric acid present in the water, and that means that all salts of carbonic acid are transformed into chlorides (these are salts of hydrochloric acid).

However, during the analysis one used too much acid because one forced the pH down to the 3.6 value. In order to be correct, one should subtract 0.065 from the value of alkalinity found. Only when measuring very soft water, this is of practical importance.

Temporary hardness of natural waters (expressed as German degrees of hardness):

South America:

- British Guyana, Mazaruni River (0.15 dry season, 0.22 rainy season).
- Cuyuni 0.33 rainy season).
- 6 blackwater creeks (0.00-0.18),
- 11 noncolored creeks (0.22-1.12),
- Barima River (1.6),
- Essequibo River (0.4),
- Demerara River (0.86 old analysis),
- Demerara River (0.11 rainy season),
- Courantyne River (0.82),
- Waini River (1.2),
- Potaro River (1.06).

Amazonas:

- Amazon River at Santarem (1.1 rainy season),
- Tapajos River (0.33 dry season, 0.2 rainy season),
- Xingu River (1.1),
- creeks in the rainforest (Terra Fime 0.00-0.44),
- upper Rio Negro (0.0).

La Plata system:

- La Plata (1.48),
- Parana River (1.62),
- Uruguay River (0.58-1.33).

Africa:

- Lower Nile (5.1-5.7),
- White Nile (7.0),
- Blue Nile (4.0),
- Lake Victoria (5.3),
- Congo Basin, 15 rivers in the eastern part of the basin (0.55-2.5),
- Congo River at Stanley Pool (0.8).

A geologist named Conway calculated a mean value of all earth's freshwaters. He found this value to be equal to 4.8 German degrees of temporary hardness. For waters that do not run from areas with marine deposits, he found a mean value of about 1.45 German degrees. As most aquarium fish in nature live in freshwaters, not in touch with marine deposits, you realize that the normal aquarium water should be soft if it is going to be "natural".