The accepted method for the determination of pH in pool and spa water uses the acid-base indicator phenolsulfonephthalein, commonly known as phenol red (Bio-Lab Test Kit No. 2 Reagent). At pH 6.8, the indicator is yellow. As the pH is increased to 8.4, the colour changes to red. In the ideal pH range for pool and spa water (7.4 - 7.6), the indicator should appear orange or slightly red.

In the presence of chlorine, bleaching of the indicator can occur. To neutralise chlorine prior to testing for pH, the Test Kit recommends addition of thiosulfate (Chlorine Neutraliser, No. 4 Reagent) to the sample. One drop is added if the free available chlorine (FAC) level is less than 3 ppm, whilst 2 drops are necessary if the FAC exceeds 3 ppm. This sample pretreatment usually suffices unless chlorine levels are excessively high. (1)

In the presence of bromine, however, phenol red may be converted to dibromophenolsulfonephthalein or bromophenol red. Like phenol red, this indicator undergoes a colour change from yellow to red as pH is increased. However, as the yellow phase
Effect of Bromine on Phenol Red in pH Tests

corresponds to a pH of 5.2, and the red to a pH of 6.8, the orange colour normally attributed to a pH of 7.4 will actually correspond to a pH of only 5.8. To further complicate matters, the bromophenol red itself may also undergo bromination to form tetrabromophenolsulphonephthalein or bromophenol blue if the bromine level exceeds 20 ppm. This indicator changes colour from yellow at pH 3.0 to blue at pH 4.6; there is no red intermediate. (2)

The consequence of these reactions to spa owners who use bromine or BCDMH is obviously of concern. If steps are not taken to prevent conversion of phenol red to bromophenol red, the pH of the spa water may be mistakenly adjusted to a much lower pH (i.e. more acidic) than ideal. Not only could this cause skin and eye irritation for bathers, but it will also accelerate corrosion of metal fittings in the spa, including heat exchanger elements. If the bromine level is high enough to convert the phenol red to bromophenol blue, the pH won't be measurable at all by the standard Test Kit method.

On the face of it, the solution to this problem should be the same as that used to counter the effects of chlorine, namely pre-treatment of the sample with thiosulfate (No.4 Reagent). This will reduce bromine to bromide, allowing phenol red to be added and pH testing to proceed as usual. Unfortunately, investigations in high levels of bromine showed that even large additions of thiosulfate may not prevent masking of the desired orange/red colour at pH 7.4 - 7.6.

Given this observation, it is recommended that bromine levels be reduced to normal operating levels before any attempt is made to determine pH using phenol red. If it is deemed necessary to determine pH in a spa high in bromine, an alternative technique must be used; a standard glass pH electrode is ideal.
Reference


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