

Analysis, Measurement and Testing Part I

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This report covers the first part of the presentation on testing methods and errors given at the 1998 NSPI Convention held in New Orleans, LA. The first part was given by Tom Seechuk of LaMotte Company while the second part was given by Neil Lowry of Lowry & Associates. This part of the presentation is entitled "DPD and Phenol Red Interferences".

Abstract: The purpose of this presentation is to define and explain chemical interferences with the DPD method used for free chlorine, total chlorine and total bromine determinations and the phenol red method for pH determinations.

Chlorine

Chloramines

There has been increasing concern about the presence of carcinogenic compounds in drinking water. Chemicals such as chloroform and carbon tetrachloride are classified as trihalomethanes and are formed by humic substances in water reacting with free chlorine. These compounds are not formed when water systems chlorinate with chloramines (combined chlorine).

The concentration of chloramines in drinking water depends on the water system. Generally concentrations of 0.5 – 4.0 ppm are used. This presents an obvious difficulty with the homeowner who fills a pool or spa with tap water. The water contains chloramines before anyone even enters. If a dealer or

service person tests this water, the high chloramines will be evident; but the tester may not be aware of an interference with the free chlorine test.

Chloramine concentrations of greater than 0.5 ppm can break through into the free chlorine reading. This will result in a higher free chlorine and lower combined reading, when in fact this is not the case.

The remedy is called the Steadifac modification. If chloramine breakthrough is suspected, add the DPD free chlorine reagents to the water and then add 5 drops of Steadifac reagent. This is thioacetamide and it "freezes" the free chlorine reading. After the free chlorine concentration is determined, a separate sample must be used for the total chlorine test.

Monopersulfate

Potassium monopersulfate (MPS) has been used for years as a non-chlorine shock in pools and spas. It is used to reduce the concentration of organics and chloramines and to produce hypobromous acid from bromide. A problem occurs in the DPD test, because MPS reacts like combined chlorine. Four years ago Dupont, makers of MPS, worked with 2 test kit companies to solve the problem.

Dupont found a chemical that could inhibit the interference of MPS. This is added after the free chlorine determination and before the total determination. The modification also allows the determination of MPS concentration.

- 1) ADD DPD # 1 and mix → free chlorine reading
- 2) ADD MPS Out and mix
- 3) ADD DPD #3 and mix → total chlorine reading

If the above is repeated without performing step 2, the total chlorine reading will contain the MPS. Subtracting the total reading with MPS Out from the total reading without MPS Out and multiplying the

result by 5 will yield ppm monopersulfate.

High Chlorine

Due primarily to concern for sanitary water, the recommended ranges for chlorine and bromine in pools and spas are increasing. DPD will bleach out at 8–10 ppm. In some cases, there may be a flash of red color around the DPD tablet, which disappears. In other cases a color may appear and then disappear. Some operators who did not know this have paid the price of adding extremely high amounts of chlorine to the water and bleaching hair and swimsuits.

There are 3 remedies:

1. One may use a dilution with tap water or deionized water. Keep in mind that tap water usually contains chlorine, so the result may be higher than it really is; Deionized water has a chlorine demand, so the result will be lower than it is. The multiplication factor to obtain the correct concentration is

1 part sample + X parts dilution water = multiplication factor.

2. One may double or triple the amount of DPD in the sample. If using liquids, be certain to add equal amounts of the liquids (i.e. 10 drops of ea., 15 drops of ea.). This will result in a color that is off-scale, but at least one will know there is chlorine or bromine present.
3. One may reduce the sample size. The amount of sample in this test is not critical. The main concern is that one is looking through the same viewpath. Whether one uses a 2 mL sample or a 10 mL sample the viewpath is the same. Again, with a reduced sample, the resulting color will be off scale, but at least one knows the halogen is there.

Reaction Time

The potable water area specifies that the DPD total chlorine test requires a 2 min. waiting time. Pool dealers and service persons do not have this time. Thus the total chlorine test may not be completely reacted when it is read.

Normally the DPD method specifies that the same sample may be used for free and total chlorine determinations. In tests comparing the addition of a #3 to a reacted #1, it was found that adding the #1 and #3 together for a total chlorine test will give more accurate results than adding these separately. Adding the reagents together resulted in up to 0.15 ppm higher result.

Other Precautions

1. Clean sample tubes.... The chemical used in total chlorine determinations is potassium iodide. It has an affinity for the plastic tubes used in testing. If the tubes are not thoroughly cleaned, the potassium iodide remaining on the tube will react in the free chlorine test yielding incorrect results. Also, do not leave a reacted chlorine sample in a sample tube. The resulting stain will be difficult to clean and will actually add to a chlorine reading.
2. Colorimeters are electronic instruments that read chlorine concentration by passing a beam of colored light through a reacted chlorine sample and reading absorbance of the light by a detector. This absorbance is translated into concentration. It is important to keep these meters clean and dry. If liquid enters the sample chamber, it can cloud the light or detector and cause incorrect readings.

pH

High Halogen

Phenol red is the indicator commonly used in recreational water pH testing. Chlorine reacts with phenol red to produce chlorophenol red; bromine reacts with phenol red to produce bromphenol blue. The difficulty arises in that chlorophenol red appears very similar to a pH 8.2 reading. Bromphenol blue can appear like a 6.8 reading on the acid side or a pH 8.2 reading on the basic side. Thus one must be cautious in obtaining such readings to ascertain if these are true readings or interferences.

Test kit companies add halogen neutralizers, either separately before adding the indicator or directly in the reagent, to eliminate the problem. Most built-in inhibitors can neutralize about 20 ppm. Above this, one would need to add a few drops of thiosulfate. When adding thiosulfate, keep in mind that to stabilize liquid thiosulfate, either sodium carbonate or sodium bicarbonate is added. Thus one may actually increase the pH of the sample by adding thiosulfate.

The pH can also be affected when using a phenol red with a built in neutralizer. Note the effect on pH the neutralizers below have, based on 10 ppm halogen samples, in simulated swimming pool water:

Inhibitor Effect

X Cl – pH lowers 0.3

Br – pH raises 0.4

thiosulfate Cl – pH raises 0.3

Br – pH raises 0.6

Y Cl – pH raises 0.2

Br – pH lowers 0.1

Thus the pH of a sample may actually change as a result of the reaction of a halogen inhibitor with the halogen. The solution to this problem is to use a combination of halogen inhibitors in the phenol red. Thus the pH does not change.

Low/High pH

The range of a pH indicator is very specific. Phenol red's range is 6.8 – 8.4. If a sample of water that has a pH of 9.0 is tested with phenol red, it will look like 8.4; if a sample of pH 4.0 is tested with phenol red, it will look like 6.8. Thus it is best to disregard readings that match the lowest or highest standard. If the reading does match the lowest or highest standard, there is a way to determine whether one is "way out" or "in the ballpark". If one adds one or two drops of acid or base demand reagent to the sample and it moves the color within the range of the comparator, it is likely the pH was close to the matched color.

Low Buffer Waters

Test kit manufacturers adjust the color of pH indicators with acid or base to the midpoint of that indicator. Phenol red is adjusted to the color of 7.6. When this is done, a slight buffering of the indicator occurs. This becomes a problem in low buffer (less than 60 ppm alkalinity) waters. Because the indicator itself has a pH of 7.6, the water may "take on" the indicator pH. If the alkalinity is low and the pH read-

ings all seem to be around 7.6, one should question these readings.

Care of pH Meters

As with many electronics, pH meters are becoming better and more affordable. However, just like any electronic device, it needs to be properly maintained. Things to keep in mind for proper pH meter maintenance are:

1. If using a meter with a separate electrode, store the electrode in the storage bottle when not in use. If using a meter such as a pocketester with a built in electrode, keep the electrode in potassium chloride or pH buffer solution, or at least tap water. Do not use deionized water, since this will ruin the electrode. Soak a piece of sponge, cotton or tissue in the storage solution and place this in the cap. Make sure that if the meter is to be stored over the off-season that it has plenty of storage solution to maintain wetness around the probe.
2. Buffer the meter daily. In testing pools or spas a one point calibration to pH 7.0 is adequate. Keep in mind that buffers have a 6 month shelf life.

About the Author

Tom Seechuck graduated with a degree in biology from Loyola College in Baltimore, Maryland. He is also a member of the NSPI's Chemical Treatment and Process Committee, and is employed by LaMotte Company in their Technical Department.