MPS Interferences in the DPD Method

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Over the past few years, two difficulties have become more evident with DPD testing: 1) The interference of monopersulfate (MPS) and 2) the inability to test high chlorine or bromine concentrations. Both problems have been solved through the use of an inhibitor chemical for the MPS and a FAS–DPD titration for high halogen concentrations.

Introduction

When MPS is used to oxidize pool or spa water, it interferes in the DPD test and gives the appearance of combined chlorine. This presents a problem for commercial facilities that are under the scrutiny of local health departments to limit combined chlorine concentration.

To better understand this, a summary of the DPD test is below:

I) DPD indicator + Fast Reactants ➔ Pink

<u>Fast Reactants</u>
Free Chlorine
Total Bromine
Iodine
Peroxide (with Molybdenum catalyst)

II) DPD #3 (KI) + Slow Reactants ➔ Darker Pink

<u>Slow Reactants</u>
Combined Chlorine
MPS
Ozone

Because MPS reacts like combined chlorine, a false reading for combined chlorine can be obtained when MPS is present.

Discussion

Eliminating MPS interference in DPD tests

DuPont, makers of MPS, have developed a chemical (known as MPS–Out) that suppresses the interference of MPS in the DPD test. When this is added to the DPD test, it eliminates the interference. Without the suppressor, a pool operator can determine the amount of MPS in the water by simple subtraction of two test results.

The modification to the DPD test is illustrated in Figure 1 on the following page.

To begin with the free chlorine test is run as usual, using either liquid or tablet DPD systems. After noting the free chlorine reading, the interference suppressor, called MPS–Out, is added and mixed. Then the DPD #3 tablet or liquid is added and the true total chlorine reading is noted.

- The free chlorine reacts with the free chlorine reagents.
- The MPS reacts with the MPS–Out.
- The combined chlorine reacts with the total chlorine reagents.

To determine the concentration of MPS,

A) test with the inhibitor
B) test without the inhibitor

5 • (B–A) = MPS concentration

Let's take an example:

Test with MPS–Out		Test without MPS–Out	
Free Reading =	1.0	Free Reading =	1.0
<u>Total reading =</u>	<u>1.2</u>	<u>Total Reading =</u>	<u>3.0</u>
Difference =	0.2	Difference =	2.0

5 • (2.0 – .2) = 9.0 ppm MPS

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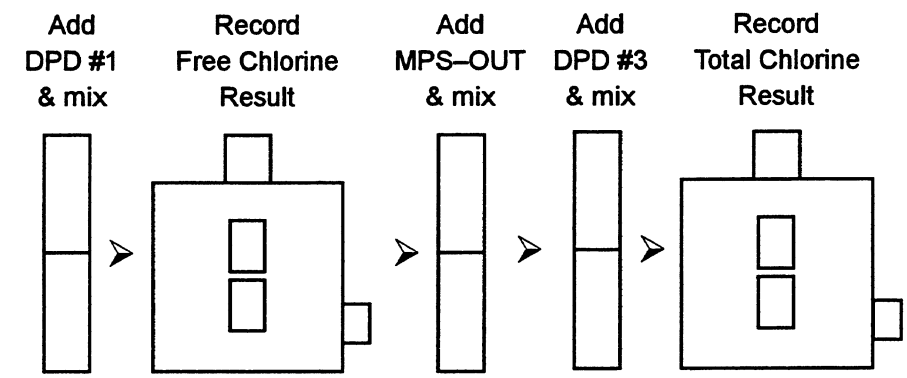

Figure 1 – DPD test sequence when utilizing MPS–OUT

Reading high halogen concentrations with the DPD test

Three factors have recently begun to play a bigger part in colorimetric halogen testing:

1) The use of higher halogen residuals and the ability to determine small combined chlorine concentrations

2) Bleaching of DPD by high halogen concentrations.

3) Inability to differentiate colors and color blindness in individuals.

Looking at a typical chlorine color comparator, one will notice that below 1 ppm, the increments between the color standards are much smaller than at higher concentrations. In the 0 – 1 ppm range, the usual increment is 0.2 ppm. Between 4 and 10 ppm, the usual increment is 1.5 – 2.0 ppm. This is because of the fundamental optics upon which colorimetric testing is based, Beer's Law.

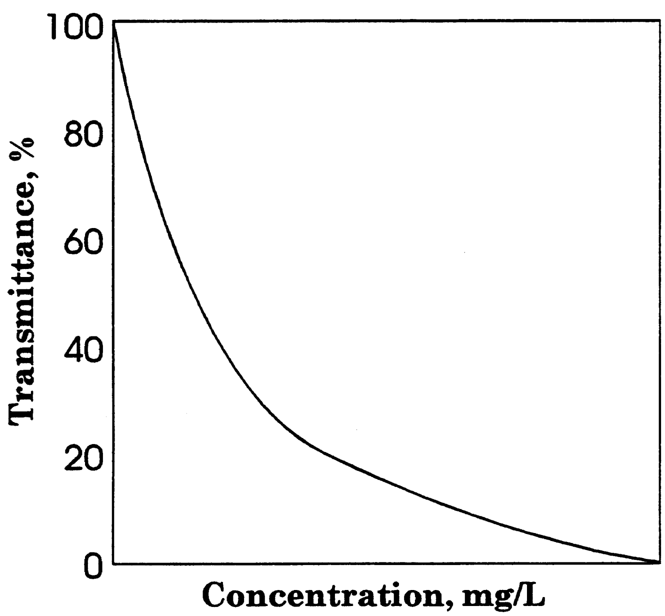

Figure 2 – Beer's Law

Essentially Beer's Law says that the more of something you have in a sample, the more color will be produced when the sample is reacted with a given reagent.

Figure 2 is a "rough" depiction of Beer's Law. The Y axis is % Transmittance (%T) and the X axis is concentration. Percent Transmittance can be thought of as a "chunk" of color which represents concentration. The chunk between 60–80%T represents a concentration band of about 0.4 ppm in the range below 1 ppm. The same 20% chunk between 0–20%T represents a 2 ppm area between 2 and 4 ppm. Thus more color variation is available in the lower concentration ranges, thereby allowing better distinction of small color differences. This is the primary reason comparators are designed as described above.

This presents a problem to an operator who is asked to maintain 2.0 ppm free chlorine and 0.4 ppm maximum combined chlorine. How does this operator decide what the concentration of the color between 2.0 and 3.0 ppm on the comparator is? It is difficult.

Although DPD is gaining in popularity as the reagent system of choice for pools and spas, one drawback is that it partially or totally bleaches out at about 10 ppm. To solve this problem, one can do one of several things – reduce the sample size, make a dilution, or add more reagent. Many companies have already reduced sample sizes on high chlorine kits. The reducing of the sample volume will not affect the results. The color one sees in a test is based on the view path of the sample tube. One could use 1 ml. instead of 5 ml. and get the same results.

One may dilute with deionized or distilled water, which will decrease the chlorine reading because of chlorine demand, or with tap water, which will increase the resulting reading because it contains chlorine. Adding 2 or 3 times the amount of reagent will

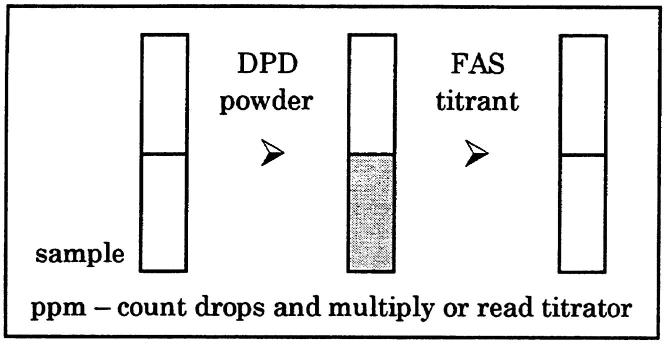

Figure 3 – FAS Free chlorine or Total Bromine test

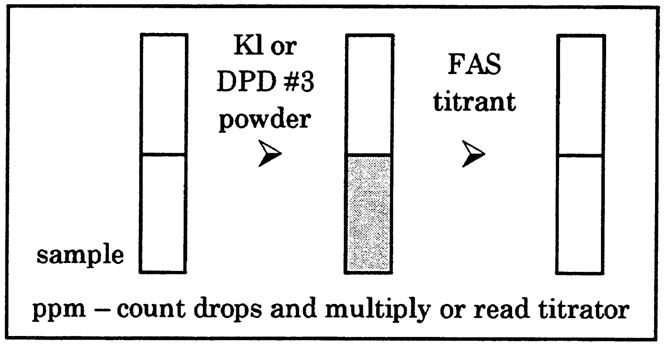

Figure 4 – FAS Total chlorine test

result in a very dark color that is off the comparator scale, but at least the operator will know there is a large concentration present.

All of the above are "band–aid" approaches to the colorimetric test problems. A better alternative is a DPD titration using Ferrous Ammonium Sulfate (FAS). This method has been widely used in the potable water area, but EPA requires that the reagent be made every day since it is unstable. However, a stable version is available for non–EPA applications such as the pool/spa area.

The test is depicted in Figures 3 and 4.

One adds a DPD powder indicator to the sample. If chlorine or bromine is present, the sample will turn pink. If a high halogen concentration bleaches out the DPD, simply add more until the pink color is stable. Then add the titrant until the pink color disappears. Determine free chlorine or total bromine concentration in the manner appropriated to the kit.

If the determination of combined chlorine is desired, add potassium iodide in the form of crystals or a DPD #3 tablet (do not use #3 liquid) to the sample that was just used for free chlorine above. If the pink color returns, combined chlorine is present. Add the titrant until the pink color disappears. This is the combined chlorine reading.

This test remedies the 3 colorimetric problems stated originally.

1) Since the titrant equivalence is usually 1 drop = 0.2 ppm, one can accurately determine chlorine concentrations with a +/0.2 ppm tolerance.
2) Since one may overload the system with DPD and still get meaningful results, the bleaching problem is eliminated.
3) Since the reaction involves a color to colorless reaction, it is quite appealing to operators who are color blind or who have difficulties with colors.

Conclusion

The MPS–Out modification and the FAS–DPD kit present two excellent alternatives to solve interferences in DPD testing.