Do You *Really* Have a Free Chlorine Residual?

Many water operators view free chlorine residual through "rose-colored" test results. Don't be duped by the pink phantom! BY ROBERT SPON

THE US ENVIRONMENTAL Protection Agency-accepted colorimetric N,N-diethyl-p-phenylenediamine (DPD) method is the most commonly used procedure to determine free chlorine residuals in water. The DPD indicator immediately reacts with free available chlorine—hypochlorous acid or hypochlorite ion—to form a pink color, which is proportional to the chlorine concentration. However, some DPD test results may be misleading because monochloramine residual interferes with DPD free analysis, creating a false-positive, phantom reading.

AVOIDING THE PINK PHANTOM

To determine chloramine or combined chlorine concentration, the total chlorine DPD method contains a special ingredient—potassium iodide—in the reagent packet with the DPD indicator. Chloramine converts the iodide reagent to iodine, which reacts with DPD to form a pink magenta color. After analysis, subtracting the free chlorine test results from the total chlorine results yields the combined chlorine concentration. However, if the free chlorine results are false positive, the calculation is flawed.

Answering the following questions will help determine if free chlorine residual is really present in your water system.

- Do you use only the free chlorine DPD test method to measure chlorine residual?
- When you pour the DPD free chlorine reagents into the water sample, do the reagents turn a faint pink color, and does the color darken with time?
- Do you wait 1 min or longer for the pink color to develop further, ensuring that you register more free chlorine residual?
- Do you have ammonia in your water supply and distribution system?
- Do you have trouble maintaining stable chlorine residuals across your distribution system?
- Do you detect a chlorine smell in the treated water? Do customers complain about the water's taste and odor?
- Is the chlorine mg/L dosage rate three to four times higher than the free residual?

If you answered "yes" to any of these questions, you may not have free chlorine residual because

- Combined monochloramine interferes with the free chlorine DPD analysis and creates a false positive or phantom reading that's artificially higher than reality. Compare the total chlorine DPD method results with your free chlorine residual and then determine the combined chlorine residual.
- Free chlorine DPD test reagents react immediately and shouldn't take time to develop color. Color drifting to darker pink is the first warning sign of chloramine interference.
- To avoid interference from combined chloramine residual, free chlorine residual should be measured within 1 min.
- If ammonia-N is present in your water supply and you form combined chloramine residual after chlorination, it isn't adequate to use only the free chlorine DPD method. Ammonia and free chlorine residual don't coexist in water.
- Free chlorine residuals are more reactive, stronger, and less long-lasting as combined chloramine residuals. If you use only the free chlorine DPD test and phantom residual is present, you have little control over system residuals, which leads to taste and odors.
- Chlorinous odors indicate dichloramine formation and combined residuals or insufficient free chlorine residual. To minimize odors, total chlorine residual should consist of >85 percent free chlorine. Stable chloramine residuals don't contain free chlorine. Free and combined chlorine aren't compatible. Free chlorine naturally decays over time during storage and reaction with pipe-scale deposits, allowing odors to develop. Chloramine residuals with unbalanced chlorine–ammonia ratio may decompose quickly, leaving taste and odor by-products for consumers.
- Ammonia (NH_3-N) creates a great demand on chlorine chemicals. About 10 mg/L of chlorine is required to

A false-positive free chlorine reading misleads operators and regulators who monitor only for DPD free chlorine. The left vial should be clear, but the color changed to pink over time because of monochloramine interference. The right vial accurately shows the DPD total chlorine residual.

PHOTOGRAPH: HACH COMPANY, USA

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consume and destroy 1 mg/L of ammonia-N before true free chlorine residual is formed. Comparing total and free chlorine, total ammonia-N, and free ammonia will help you determine your location on the breakpoint curve (see figure, page 27). High total chlorine and low free chlorine residual, in the presence of ammonia, is the second warning sign of phantom free chlorine residuals.

PHANTOM RESIDUALS

The free chlorine DPD method immediately measures free chlorine residual—hypochlorous acid (HOCl) and hypochlorite ion (OCl^-)—in water samples. If only combined chloramine—monochloramine (NH_2Cl)—is present, interference will occur and increase within seconds to minutes when free DPD reagents are used. This interference causes false-positive free chlorine results, leading water operators to assume they have free chlorine residual when they really don't. High monochloramine residual (1–4 mg/L NH_2Cl) generates pink-colored interference using the free chlorine DPD reagents. Because many state guidelines suggest that groundwater systems measure only free chlorine via the DPD method and maintain a trace of free chlorine (0.2–0.3 mg/L) in the ends of their system, operators are deceived into thinking they have adequate free chlorine residual when they see a faint pink phantom color. The DPD free chlorine reagents may develop a phantom reading that ranges from faint pink (0.1–0.3 mg/L) immediately to dark magenta (1.0^+ mg/L) over time, depending on how much monochloramine is in the water sample.

Bromine, iodine, chlorine dioxide, ozone, oxidized manganese, potassium permanganate, and monochloramine have been identified as substances that interfere with analysis if the free chlorine DPD method is used. Sample temperature, relative concentration of monochloramine to free chlorine (if present), and the time required to perform the analysis are primary risk factors contributing to the intensity of interference. Table 1 shows typical interference levels from monochloramine (NH_2Cl) residual, after a 1-min hold time for color development.

Phantom chlorine residuals are easy to identify at the water plant or well

Table 1. Monochloramine Interference on Free Chlorine DPD Analysis

Sample temperature influences interference levels from monochloramine residual. Shown here are typical interference levels after a 1-min hold time for color development.

Monochloramine Level *mg/L*	Water Temperature 5°C (40°F)	Water Temperature 10°C (50°F)	Water Temperature 20°C (68°F)	Water Temperature 30°C (86°F)
NH_2Cl Residual	DPD-free bias	DPD-free bias	DPD-free bias	DPD-free bias
1.2 mg/L as Cl_2	+0.15	+0.19	+0.29	+0.30
2.5 mg/L as Cl_2	+0.35	+0.38	+0.55	+0.61
3.5 mg/L as Cl_2	+0.38	+0.56	+0.69	+0.73
5.0 mg/L as Cl_2	+0.68	+0.75	+0.93	+1.05

PHANTOM FREE CHLORINE CHECKLIST

If any of these indicators exist in your water system, consider the following steps for corrective action.

- To learn if phantom free residuals exist, perform a DPD free chlorine test, record the immediate reading, and observe the sample color for several minutes. If the sample drifts to darker color and higher readings, monochloramine is present in the sample and free chlorine readings are phantom.
- To determine the cause of the problem, analyze raw and treated water for ammonia, and analyze treated water for monochloramine.
- Calculate the following: free ammonia mg/L = ammonia-N mg/L – monochloramine-N mg/L, or use the combination test to measure monochloramine and free ammonia-N.
- To identify the location of your chlorine residual on the breakpoint curve (see figure, page 27), calculate your chlorine dosage and demand (Table 2). Then project the approximate value on the breakpoint curve.

house after additional testing (see Phantom Free Chlorine Checklist, above). However, authentic free chlorine residuals from one water source may convert to phantom residuals in the distribution system after blending with chloramine residuals from other water supplies. Uncontrolled blending of free chlorine residual and chloramine creates a diluted and potential odor-causing dichloramine residual. Tracking ammonia, monochloramine, and free ammonia concentrations across the distribution system will expose the extent of phantom residuals and interference with true free chlorine results.

Table 2. Chlorine Demand Calculations*

Calculate your chlorine dosage and demand using the instructions below, then project the approximate value on the breakpoint chlorination curve on page 27.

Water Quality Parameter *mg/L* (example)	Residual Demand (x Factor) =	Total Chlorine Demand *mg/L*
Iron 0.3 mg/L	x 0.64 mg/L =	0.192 mg/L
Manganese 0.05 mg/L	x 1.30 mg/L =	0.065 mg/L
Hydrogen Sulfide 0.2 mg/L (optional factor) 0.2 mg/L	x 2.08 mg/L to S = x (8.32 mg/L to SO_4)	0.416 mg/L (1.664 mg/L)
Nitrite-N 0.1 mg/L	x 5.0 mg/L =	0.5 mg/L
Ammonia-N 0.1 mg/L	x 9–11 mg/L = Cl_2 by weight	1.0 mg/L
Organic-N mg/L 0.05 mg/L	x 1 mg/L =	0.05 mg/L
Total Organic Carbon (TOC) 1.0 mg/L	x 0.1 mg/L =	0.1 mg/L
Chlorine dosage mg/L = (lb/day) x (% active) / (8.34) x (MGD) **(Chlorine dose > total demand = free residual mg/L)** **(Chlorine dose < total demand = combined residual mg/L)**		**= 2.323 mg/L total demand**

***How to Use this Table:** Insert into a table the value for each possible reducing agent (iron Fe^{+2}, manganese Mn^{+2}, hydrogen sulfide, nitrite-N) and combining agent (ammonia-N, organic nitrogen, TOC) that is in your source water. Use the multiplier factor to calculate the chlorine demand for each contaminant. The total chlorine demand is an approximate value used to project an optimal chlorine dosage to reach the breakpoint at which free chlorine residual is available. Raw water pretreatment, aeration, and oxidation with other water treatment chemicals will offset and reduce the calculated chlorine demand. If your chlorine dosage is greater than the total demand, it's likely the breakpoint has been achieved and free chlorine residual is available. If the chlorine dosage mg/L is less than the demand, combined chloramine remains in the water and free chlorine hasn't formed yet.

AMMONIA CONTAMINATION

The presence of naturally occurring ammonia (NH_3-N) is an unregulated nitrogen contaminant often found in shallow- and deep-well groundwater supplies and seasonally found in surface water supplies in the United States. Fertilizer runoff, septic tank seepage, sewage, erosion, and decay of natural deposits are considered typical sources of ammonia contamination in water. However, because ammonia isn't on the USEPA Primary Drinking Water Regulations list of contaminants that present health risks, water operators aren't required to routinely determine if ammonia exists in their water supplies. Unfortunately, the regulated and required analysis of nitrite-N (1 mg/L MCL as NO_2-N) and nitrate-N (10 mg/L MCL as NO_3-N) contamination also creates a false sense of security, leading many operators to falsely assume that—if nitrite–nitrate is absent or low in their water supply and system—ammonia is also absent.

Because the decomposition of ammonia (nitrification) is a sequential process, the end by-product formation of nitrate indicates a loss or absence of ammonia in a closed system. Ammonia–nitrite–nitrate concentrations in water balance on a sliding scale in a ratio of 1:1:1. Each compound (NH_3-N, NO_2-N, NO_3-N) measured as nitrogen (-N) is limited by the quantity of the other remaining form. Nitrite-N carries the lowest maximum contaminant level (MCL) of 1 mg/L. Therefore, 1 mg/L of ammonia-N is a practical maximum limit that should be considered a secondary drinking water standard. Although naturally occurring ammonia doesn't create a direct cosmetic or aesthetic problem for consumers, it contributes to

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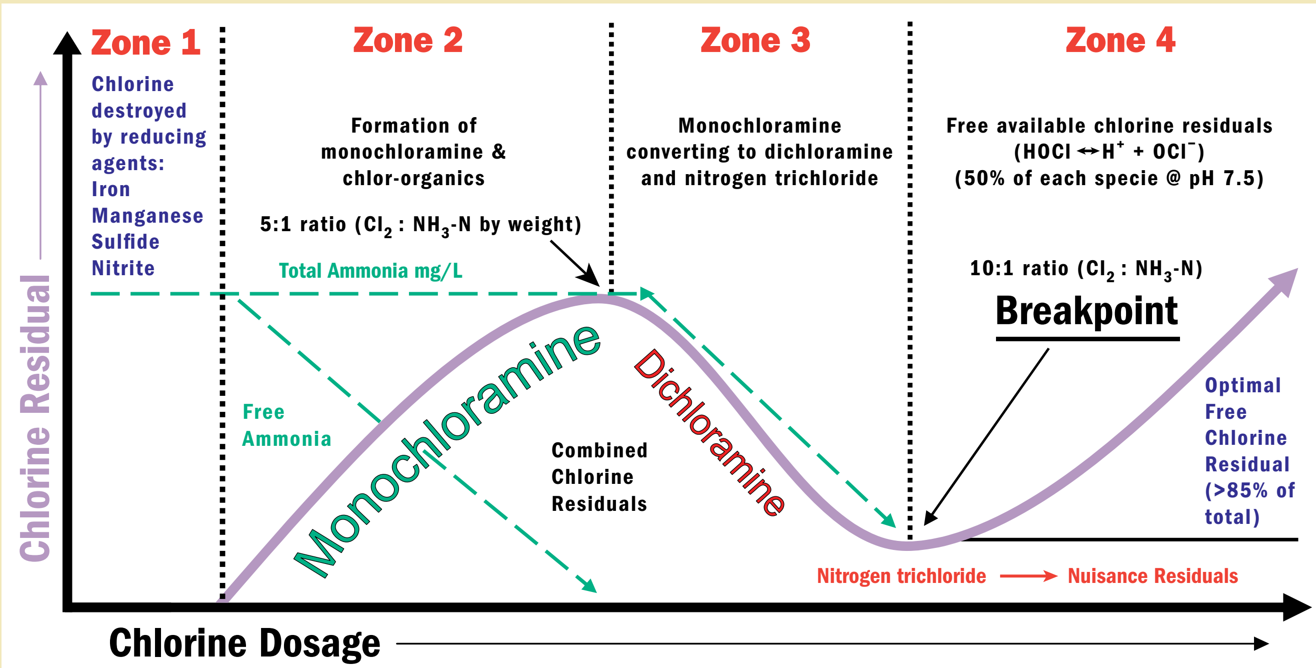
Breakpoint Chlorination Curve Interpretation*

Comparing total and free chlorine, total ammonia-N, and free ammonia will help you determine your location on the breakpoint curve.



***Zone 1:** Initial chlorine demand is caused by reducing agents (Fe^{+2}, Mn^{+2}, H_2S, NO_2^-) that consume most of the chlorine applied prior to forming combined residuals.

Zone 2: Additional chlorine combines with available total ammonia and reactive organics until forming maximum monochloramine residual. At the same time, uncombined free ammonia is being depleted until it reaches zero.

Zone 3: More chlorine dosage converts monochloramine into odorous dichloramine and nitrogen trichloride. Total combined chloramine residual decreases and ammonia concentration approaches zero at the breakpoint.

Zone 4: True free chlorine residual is obtained and provides the least nuisance odor when free residuals make up 85 percent of the total chlorine concentration. Nuisance combined chlorine residuals survive and the potential for disinfection by-products (trihalomethane and haloacetic acid) formation remains, as free chlorine residual develops further.

chlorinous taste and odors or nitrification when chlorine–ammonia ratios are out of balance in the water system.

The USEPA maximum residual disinfectant level (MRDL) of 4.0 mg/L disinfectant residual limits public exposure to chlorine in drinking water systems on a running annual average. Therefore, water systems practicing intentional chloramination will always dose less than 1 mg/L of ammonia-N chemical to remain below the MRDL chlorine residual and also avoid excess free ammonia. Many US groundwater supplies contain ammonia-N of >1 mg/L and are unable to avoid free ammonia and nitrification without excessive chlorine dosage (>10 mg/L). Without the proper ratio between chlorine dosage rate and ammonia (optimal at ≈ 5:1 parts Cl_2: NH_3-N), the formation of unstable combined chloramine residual is inevitable. Lack of optimal monochloramine residual (> 2.5 mg/L) in water systems results in nitrification (loss of chlorine residual, consumption of NH_3, formation of NO_2, ORP/pH/alkalinity depression), loss of water quality, chlorinous taste and odor, biofilm regrowth, microbial corrosion, color, and turbidity. Without ammonia contamination in their water supply, operators can maintain optimal free chlorine residuals (85 percent of total residual) in their water system, resulting in less chlorinous odor.

PRACTICAL CONSIDERATIONS

To avoid being duped by a false-positive reading, review the Phantom Free Chlorine Checklist, page 26. Also, remember to calculate your chlorine dosage and demand (Table 2), refer to the breakpoint curve shown in the figure above, and maintain the optimal chlorine (monochloramine or free) residual in your water system. Equipped with these new tools, you can respond confidently when asked if you really have a free chlorine residual.