Advances in Chlorine Testing

By Ivars Jaunakais

New technologies improve testing for common disinfectant

Water is the most important natural resource in our environment, and it is used daily. If water was a pure substance it could be used without concern—but water is far from pure. It contains microorganisms and dissolved minerals, both of which need to be controlled before water can be used safely. Because of its effectiveness against a broad range of microorganisms, chlorine is the primary disinfectant used.

The main reason for drinking water disinfection is to create safe, potable water. Chlorine has been used for public health for more than a century. In 1908, Jersey City, N.J., and Chicago began to routinely treat water with chlorine. Today, more than 80,000 tons of chlorine are used each year in the U.S and Canada to disinfect drinking water.

Chlorine Disinfection 101

The Chick-Watson Relationship states that at a given temperature the disinfection rate by chlorine is predictable for each type of microorganism. For example, a one-minute contact time is required for inactivation of *E. coli* bacteria using a 1-mg/L dose of hypochlorous acid (HOCl). Figure 1 features a list of several pathogens that can be transmitted in water and their inactivation times with 1 part per million (ppm) chlorine. In actual practice, the contact time is influenced by engineering constraints such as water tank size, rate of water circulation, turnover, temperature and levels of organic contaminants.

As shown in Figure 2, chlorine is available from a variety of sources. Despite their chemical and physical differences, they all form hypochlorous acid when added to water. Hypochlorous acid is the actual disinfecting agent. Because each version of chlorine forms the same disinfecting agent, the same test method can be used for all of them.

Two chemical reactions impact the performance of chlorine (as hypochlorous acid) as a disinfectant. The first is its reaction with a hydroxide ion (OH^-), which is readily available in an aqueous solution with a pH level above 7, to form a hypochlorite ion (OCl^-). Figure 3 illustrates pH versus chlorine species. A hypochlorite ion is less than one-third as effective as a disinfectant as hypochlorous acid. The sum of hypochlorous acid and hypochlorite ions is called free chlorine. Their chemical relationship is shown in Figure 4.

The second chlorine reaction is with ammonia (NH_3) and organic nitrogen compounds such as proteins and amino acids in the water to form chloramines. A series of reactions occur to form the chloramines: monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and nitrogen trichloride (NCl_3). Chloramines typically impart an unpleasant taste and odor to the water and they are less effective as a disinfectant. Active chlorine can be transferred from inorganic chloramine to amine-containing (organic) compounds. Monochloramines are most often found in water with a pH between 7 and 7.8. The sum of the chloramine species is called combined chlorine. It is chemically described in Figure 5.

The process that ultimately destroys both the combined chlorine and the organic compounds responsible for it is called breakpoint chlorination. In water treatment facilities, breakpoint determination is necessary for proper treatment to make water suitable for drinking.

Another common term is total chlorine, defined as the sum of free chlorine and combined chlorine. In some cases, after treating the water with chlorine, water treatment facilities add ammonia to neutralize the chlorine. This is used to keep trihalomethane compounds within U.S. Environmental Protection Agency (EPA) limits to protect health and keep the water within EPA specifications.

Testing Options

Using a particular chlorine test method for drinking water testing is not a guarantee for quality results. To achieve good test results, the analytical test should meet the following goals:

- The test is generally accepted (meeting compliance requirements when the application requires them) and appropriate for the staff's technical ability;
- The test is robust, using reagents and equipment that are reliable and stable; and
- The test is not affected by interferences and is accurate when staff performs the test correctly.

Five basic EPA-accepted methods measure free chlorine concentrations:

- Amperometric method;
- DPD-FAS titrimetric method;
- DPD colorimetric method;
- Syringaldazine (FACTS) colorimetric method; and
- TMB (3,3',5,5'Tetramethylbenzidine) SenSafe Aperture Colorimetric Test Strip method.

The commonly used DPD colorimetric method works by determining the chlorine concentration from the intensity of the color formed when the chlorine reacts with DPD, a color-forming indicator. The DPD-FAS titrimetric method determines the chlorine concentration for a known volume of water by measuring the amount of FAS titrant needed to bleach out the DPD-chlorine color formed. This DPD

Figure 1. Disinfection Rates

Pathogen	Inactivation Time
E. Coli 0157:H7 Bacterium	Less than 1 minute
Hepatitis A Virus	About 16 minutes
Giardia Parasite	About 45 minutes
Cryptosporidium Parasite	About 15,300 minutes (10.6 days)

Figure 2. Chlorine Sources

Chemical Name	Chemical Formula	Form	% Chlorine
Chlorine Gas	Cl_2	Gas	100%
Calcium Hypochlorite	$Ca(OCl)_2$	Solid	65% - 70%
Sodium Hypochlorite	NaOCl	Liquid	~12%

Figure 3. Percent HOCl and OCl⁻

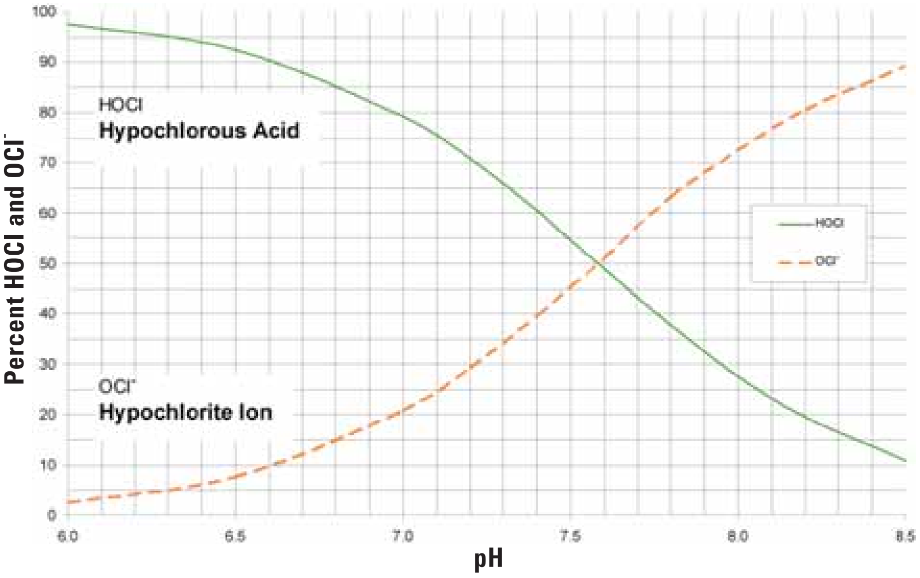

Figure 4. Chemical Relationship of Free Chlorine

$$HOCl + OH^- \rightleftharpoons OCl^- + H_2O$$

Figure 5. Chemical Relationship of Combined Chlorine

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$$
$$HOCl + NH_2Cl \rightarrow NHCl + H_2O$$
$$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$$
$$HOCl + \text{organic nitrogen} \rightarrow R\text{-}NHCl + H_2O$$
$$HOCl + R\text{-}NHCl \rightarrow R\text{-}NHCl_2 + H_2O$$

test is relatively quick, simple and has enjoyed widespread use, but recently it is being replaced by more convenient and stable DPD methods.

A variety of DPD tests are available from manufacturers such as Hach Co., Palintest Ltd., LaMotte Co., HF Scientific Inc., Orbeco-Hellige and Industrial Test Systems Inc. The various DPD tests deliver the DPD reagents as tablets, powder pillows, reagent strips or liquid reagents. These can be used in a colorimeter or as part of the DPD-FAS titrimetric method to determine the chlorine concentration.

The latest DPD methodology for drinking water testing uses DPD reagent strips in combination with a colorimeter, which has the sample cell permanently sealed in the meter. The colorimeter is waterproof and offers several benefits that make it more convenient than traditional colorimetric DPD chlorine test methods. The quick, non-technical method does not require a cell or test tube and the reagent strips do not require any preparation or measurements prior to the test.

For proper water testing, maintenance and/or monitoring of free and total chlorine concentrations, selecting the best and most convenient test method needs some consideration. Fortunately, today's professionals have many convenient and cost-effective options. Chlorine disinfection, aided by advances in testing, will continue to safeguard human health. *wqp*

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