



Evaluation of different methods for determination of properties of chlorine-based sanitizers

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ABSTRACT

Chlorine-based sanitizers, such as electrolyzed oxidizing (EO) water, are used for the sanitation of food contact surfaces and the prevention of cross contamination in various food processing settings. Several different chlorine species are present in EO water, and these chlorine species are important to the antimicrobial efficacy. Measurements of free and total chlorine, hypochlorous acid (HOCl), hypochlorite ion (OCl^-) and chloride were conducted on chlorinated water and EO water solutions using a variety of commercially available methods. The chlorinated and EO water solutions differed by pH, initial free chlorine concentration, chloride concentration and organic compound concentration. It was discovered that these factors influenced the methods used to measure the various chlorine species by differing amounts. The data from this study will help in determining the appropriate methods of measuring free chlorine, total chlorine and chloride in chlorine-based sanitizers under various conditions.

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1. Introduction

Chlorine-based sanitizers, such as electrolyzed oxidizing (EO) water, have been used in a variety of applications to control the spread of pathogenic organisms. Due to the reactive nature of chlorine, the nature of the chlorine species in solution could be different in one chlorine-based sanitizer than in another. In order to gain more understanding of the quality of EO water, it is important to know all significant forms of chlorine in solution. Forms of chlorine that are significant in EO water include free chlorine, bound chlorine, total chlorine, chloride ion and hypochlorous acid to hypochlorite ratio.

Free chlorine refers to the chlorine that is available for disinfection and is not bound to organic compounds (Nakajima et al., 2004). In this case, free chlorine could refer to hypochlorous acid (HOCl), hypochlorite (OCl^-) and chlorine (Cl_2). There are several methods useful for estimating free chlorine, and one of the frequently used methods is a titration involving N,N-diethyl-p-phenylenediamine (DPD) and ferrous ethylenediammonium sulfate (FEAS). The DPD-FEAS method has been used in several studies (Guentzel, Lam, Callan, Emmons, & Dunham, 2008; Kim, Hung, & Brackett, 2000; Kim, Hung, Brackett, & Frank, 2001; Len, Hung, Erickson, & Kim, 2000) as the method of free chlorine determination. The method has a detection range of 0–3.5 ppm, so

it is necessary to dilute solutions with high chlorine content to fit in this titration range. In the assay, free chlorine oxidizes DPD to form a magenta color, which is the result of a free radical known as a Würster dye (Zarei & Sovizi, 2011). The magenta species is then reduced back to DPD by FEAS upon titration. In addition to titration with FEAS, free chlorine can be quantified spectrophotometrically using a DPD color change standard curve. This method has a similar range to the titrimetric method, with the added benefit of being quicker and more objective.

Bound chlorine refers to chlorine that has reacted with organic compounds, forming an organohalide. One of the most common organohalides formed in the presence of proteins and amino acids are chloramines. Chloramines can be estimated by a variety of methods. One such method is the so-called indophenol method developed by the Hach Company. This method is a colorimetric method in which monochloramine reacts with a substituted phenol to form a monoamine intermediate, which then reacts with excess substituted phenol to form green-colored indophenol. Other methods for detection include methods that utilize chromatographic separation followed by various detection schemes, such as flame ionization (Steverink & Steunenberg, 1979) and amperometric detection (Ge, Wallace, & O'Halloran, 1990). Total chlorine refers to the sum of bound chlorine and free chlorine, and can be calculated using the DPD-FEAS method as well as the DPD spectrophotometric method.

Despite the usefulness of the DPD-FEAS method in determining free chlorine, the assay cannot differentiate one component of free chlorine from another. It has been shown that both HOCl and OCl^-

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can be determined quantitatively by UV spectroscopy (Morris, 1966). HOCl absorbs UV light at 234 nm best, and OCl^- absorbs UV light at 292 nm best. The HOCl and OCl^- concentrations can then be calculated from the absorbance readings using the Beer's Law equation below:

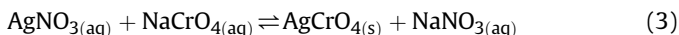
$$A = \epsilon bc \quad (1)$$

Where "A" is absorbance. "b" and "c" are light path length (cm) and concentration (in M), respectively, and " ϵ " is molar absorptivity ($\text{M}^{-1} \text{cm}^{-1}$). The molar absorptivities of HOCl and OCl^- are 100 and 350, respectively (Morris, 1966). The main weakness to the UV method is that the method is prone to interference from other species. For example, the presence of ferrous sulfate results in much higher than expected absorbance readings for HOCl and OCl^- .

Chloride ion (Cl^-) concentrations are an important consideration in EO water for several reasons. The conversion efficiency of an EO water generator is determined by the concentration of chloride ions and can be measured by means of a titration involving silver nitrate. Silver nitrate reacts with chloride as follows in Equation (2):



The titration endpoint is marked when all the Cl^- has reacted with silver. After that, silver reacts with chromate to form a red-colored compound as follows:



An alternate method of chloride determination is a reaction with mercuric thiocyanate ($\text{Hg}(\text{SCN})_2$) in the presence of ferric ions. Chloride reacts with $\text{Hg}(\text{SCN})_2$ to form mercuric chloride, and iron reacts with thiocyanate to form ferric thiocyanate, which can be detected at 254 nm (Zall, Fisher, & Garner, 1956).

The purpose of this study is to identify best methods of chlorine species determination using sodium hypochlorite solution as the standard (with initial pH at alkaline range) and evaluate the effect of pH, chloride content, initial chlorine concentration and organic addition on chlorine species determination. Methods identified were then used to evaluate whether they are also appropriate for EO water with an initial pH at acidic range.

2. Materials and methods

2.1. Sodium hypochlorite sample preparation

Twenty four different 1 L 20 mg/kg and 40 mg/kg initial free chlorine samples were made by adding 0.4 ml/L and 0.8 ml/L, respectively, of 5% NaOCl (Ricca Chemical, Arlington, TX, U.S.A.) into deionized water. The pH of the samples was adjusted to 2.5, 6.0 and 9.3 using 1 N and 0.1 N HCl. Known concentrations of chloride (200 mg/kg and 600 mg/kg) were added to the chlorinated water samples in the form of NaCl. The NaCl was added in addition to the chloride already present in solution. Organic materials were added in the form of 20 mg peptone to the 40 mg/kg initial chlorine sample and 10 mg peptone to the 20 mg/kg initial chlorine sample. Samples containing peptone were capped and placed in a lightless environment without agitation at room temperature for 1 h before measurements were conducted. Samples without organics were measured immediately after preparation.

2.2. Treatment conditions and parameter measurement

Total chlorine, free chlorine, HOCl and OCl^- and chloride measurements were performed on each sample within 30 min after

preparation (in the case of peptone-free samples) or after 1 h in samples with peptone added. Chlorine loss on each sample was minimized as the tests are performed by sealing the containers and placing them in a dark environment while they were awaiting measurement.

Free chlorine and total chlorine were measured by the DPD-FEAS titrimetric method (Hach Company, Loveland, CO, U.S.A.). For the DPD-FEAS method, a 5 ml sample was taken from each sample, and the volume was adjusted to 100 ml with deionized water. The volume was split into four 25 ml samples. Two of the 25 ml samples were used in free chlorine tests while the other two were used in total chlorine tests. The contents of a DPD free or total chlorine reagent packet (Hach Company, Loveland, CO, U.S.A.) were added to each sample under agitation. The free chlorine tests were measured immediately by titrating with a cartridge of 0.00564 N ferrous ethylenediammonium sulfate (FEAS) (Hach Company, Loveland, CO, U.S.A.) via digital titrator. The total chlorine tests were allowed to sit for 3 min before being titrated with FEAS. The result on the digital titrator was multiplied by 0.2 to yield a result in mg/L.

Free chlorine and total chlorine were also measured by the DPD colorimetric method (Hach Company, Loveland, CO, U.S.A.). For this method, 5 ml of sample was added to 495 ml of deionized water. The diluted sample was distributed to 4 beakers (25 ml/beaker) so that 2 total chlorine and 2 free chlorine tests could be performed. A portion of the diluted sample was also used as a blank for a DR/890 colorimeter measurement (Hach Company, Loveland, CO, U.S.A.). DPD total and free chlorine ACCUVAC ampules (Hach Company, Loveland, CO, U.S.A.) were used to collect portions of the diluted sample in the beakers for testing. Free chlorine tests were read in the colorimeter immediately after mixing while the total chlorine tests were allowed to sit for 3 min. The results were reported as mg/L.

Chloride was measured by the silver nitrate titrimetric method (Hach Company, Loveland, CO, U.S.A.). Each sample was diluted 1:5 using deionized water. The contents of a chloride 2 indicator powder pillow (Hach Company, Loveland, CO, U.S.A.) were added to 100 ml of diluted sample and allowed to mix. The samples were then titrated to an endpoint (brown color) using 1.128 N silver nitrate cartridges (Hach Company, Loveland, CO, U.S.A.) dispensed using a digital titrator. The number on the titrator was multiplied by 2.5 to yield a concentration measurement in mg/L.

Chloride was also measured by the mercuric thiocyanate spectrophotometric method (Hach Company, Loveland, CO, U.S.A.). One ml of sample was diluted 1:100 with deionized water. Two ml of mercuric thiocyanate solution (Hach Company, Loveland, CO, U.S.A.) and 1 ml of ferric ion solution were added to 25 ml of the diluted samples. After 2 min, each mixture was read using a DU 520 UV/Vis spectrophotometer (Beckman Coulter Inc., Brea, CA, U.S.A.) at 455 nm. Deionized water was used as a blank, and the absorbance readings for the samples were related to concentrations using a standard curve constructed using samples of salt water with known chloride concentrations. Chloride was also measured by a Cl^- ion probe. An Orion 9617BNWP Chloride Combination Electrode (Thermo Fisher Scientific Inc., Waltham, MA, U.S.A.) was used in the chloride measurements. The probe output was read on an Accumet® AR50 Dual Channel pH/ion/conductivity meter (Thermo Fisher Scientific Inc., Waltham, MA, U.S.A.). Results were displayed in ppm.

HOCl and OCl^- were measured spectrophotometrically. The concentration of HOCl and OCl^- was determined using the Beer's Law relationship mentioned previously. The same UV/Vis spectrophotometer mentioned above was used to measure HOCl at 234 nm and OCl^- at 292 nm. Quartz cuvettes were used, and the path length was measured to be 1 cm. The molar absorptivities of HOCl and OCl^- were 100 and 350, respectively. The results were reported in mg/L.

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