Quality Control of Sodium Hypochlorite (NaOCl) Solutions by Density Measurement

Relevant for: Drinking Water Providers, Public Swimming Pools Operators, Public Hygiene

A density-based concentration check of sodium hypochlorite - disinfectant for drinking water and swimming pools and used for sanitation of rooms and objects - avoids ineffective disinfection and litigations with suppliers.

Figure 1: Drinking water

1 Introduction

Drinking water treatment

The water treatment industry is growing rapidly due to the increasing population that leads to a need for safe drinking water.

The World Health Organization (WHO) has been concerned with health aspects of the management of water resources for many years and publishes various documents concerning the safety of the water environment and its importance for health. The message is clear: **All water supplies should be disinfected** [1].

This provides a growing demand for disinfectants.

At present, the principal disinfectant used worldwide is chlorine; although alternatives are being increasingly investigated and processes such as ozonation are becoming more common.

Chlorine is generally the disinfectant of choice as it is reasonably efficient, cheap and easy to handle. In all but the smallest water treatment plants, chlorine is added to water as either in aqueous solution (usually sodium hypochlorite, NaOCl) or chlorine gas. The recommended concentration of NaOCl in water can vary between 0.5 mg/L and 2.0 mg/L.

Other disinfectants include ozone, ultraviolet light and iodine. These all have disadvantages. UV is not a particularly effective disinfectant and it is difficult to expose water for sufficient time for disinfection to be effective. Neither ozone nor UV provide a residual disinfectant and therefore offer no protection against recontamination in distribution. Both iodine and ozone are carcinogenic. There are also significant health and safety concerns, for operators, regarding the generation and application of ozone and chlorine (especially in the gaseous form). Iodine can also lead to thyroid problems with pregnant women and is generally more toxic than chlorine.

Public swimming pools treatment

The risk of illness or infection associated with swimming pools and similar recreational water environments is also of big importance. Many of the outbreaks related to pools have occurred because disinfection was not applied or was inadequate.

The control of viruses and bacteria in swimming pool water is usually accomplished by appropriate treatment, including filtration and the proper application of chlorine or other disinfectants.

The chemical disinfectants that are used most frequently include chlorine as a gas and as hypochlorite [2]. Recommended concentration of NaOCl in water can vary between 1.0 mg/L and 4.0 mg/L depending on country specific regulations.

Sterilization of rooms/objects

Sanitizer containing NaOCl is recommended by several institutions including WHO and CDC as a cheap but effective disinfectant for rooms and objects, which are infected by bacteria and viruses [3]. The NaOCl sanitizer requires 5 to 10 minutes of contact time to inactivate microorganisms.

In light of the Coronavirus pandemic, various state governments in India, for instance, conducted sanitizing drives, disinfecting the streets with solutions containing sodium hypochlorite [4].

The worldwide recommended (by WHO) concentration of NaOCl solutions in water for sanitation is 0.1 %.

2 Sodium hypochlorite, NaOCl

General information

Sodium hypochlorite (NaOCl) is an efficient, cheap and easy to handle disinfectant.

This compound is a water solution containing about 1 to 18 % “active chlorine”, which is disinfectant, algaecide, fungicide and microbicide.

The solution must be stored carefully to prevent deterioration and it can cause burns in contact with skin.

Legislation

NaOCl is worldwide recommended (WHO) and allowed (including the European Union and US EPA) as disinfectant for drinking water, swimming pools and sanitations of rooms/objects.

US: According to the FDA list of regulated substances 40 CFR §68.130, **sodium hypochlorite is not a regulated substance** therefore, no “active chlorine” concentration check is requested [5], as long as the recommended dilutions are respected.

EU: The European Union has a drinking water policy, the Directive EC No 1451/2007 [6] that established the minimum standards for water intended for human consumption. The Directive includes disinfectants and disinfecting by-products limits similar to those recommended by WHO. As in the case of the American legislation, sodium hypochlorite does not need “active chlorine” checks.

Preparation of NaOCl

NaOCl is the product of the chlorination of soda, NaOH, according of following reaction:

$Cl_2 + 2\,NaOH \rightarrow NaCl + \mathbf{NaClO} + H_2O$ (1)

The Hooker process is the only large-scale industrial method of sodium hypochlorite production. In the process, sodium hypochlorite (NaClO) and sodium chloride (NaCl) are formed when chlorine, in gas form, is passed into cold dilute sodium hydroxide solution. The solution must be kept below 40 °C (by cooling coils) to prevent the undesired formation of sodium chlorate [7].

The chemistry behind the disinfection

Sodium hypochlorite dissociates in water (equation 2) and its ion OCl^- hydrolyzes to hypochlorous acid (HClO) according to equation (3):

$NaOCl \rightarrow Na^+ + OCl^-$ (2)

$OCl^- + H_2O \leftrightarrow HClO + OH^-$ (3)

NaOCl solutions are fairly alkaline, with pH 11 or higher since hypochlorous acid is a weak acid. Usually, a solution of hydrochloric acid is added in order to decrease the pH value to an optimum range (~7) at the moment of use.

Hypochlorous acid participates in the following equilibrium with chlorine (Cl_2):

$HClO + H_3O^+ + Cl^- \leftrightarrow Cl_2 + 2H_2O$

The ratio of $Cl_2/HClO/ClO^-$ is pH and temperature dependent. HOCl is predominant in the pH range 2 to 7 [8].

<u>The undissociated hypochlorous acid (HOCl) acts as a disinfectant.</u>

Improper use of NaOCl, including deviation from recommended dilutions (either stronger or weaker), may reduce its effectiveness for disinfection and can result in injury.

Available Chlorine (Cl_2)

Before the development of sodium hypochlorite solutions, chlorine was used directly for disinfecting, bleaching and oxidizing. With the storage advantages of an aqueous solution, sodium hypochlorite solutions have replaced chlorine in many of these typical end uses [8].
In order to understand how much chlorine (Cl_2) is available in a sodium hypochlorite (NaOCl) solution, consider the equation (4) and (5).

$NaOCl + 2KI + 2HAc \rightarrow I_2 + NaCl + 2KAc + H_2O$ (4)

$Cl_2 + 2KI \rightarrow I_2 + 2KCl$ (5)

A mole of sodium hypochlorite oxidizes the same amount of iodide as a mole of chlorine. Considering that the molecular weight of NaOCl is 74.5 g/mol and the one of chlorine (Cl_2) is 71 g/mol, the “available chlorine” can be calculated as ratio of 74.5/71=1.05.

These are the typical units to express the concentration of a sodium hypochlorite solution [9]:

- **“% Sodium Hypochlorite”** (w/w)
- **“% Active Chlorine”** (w/v)
- **“g/l Active Chlorine”** (grams of Active Chlorine/liter of sodium hypochlorite solution)

Conversion from w/w to w/v concentration needs to consider density.

Titration is the method to determine the concentration of NaOCl (and consequently %Active Chlorine) any time. The method is slow, complex and needs qualified staff.

In case of fresh samples we recommend the density measurement to determine the concentration of NaOCl, which is fast, accurate and doesn´t need qualified staff.

Deterioration of NaOCl

Unfortunately, the concentration of NaOCl varies during the storage due to an aging/deterioration process according to the equation (6):

$$3\ NaOCl\ (aq) \rightarrow 2\ NaCl\ (aq) + NaClO_3\ (aq)$$

This deterioration is temperature dependent [10].

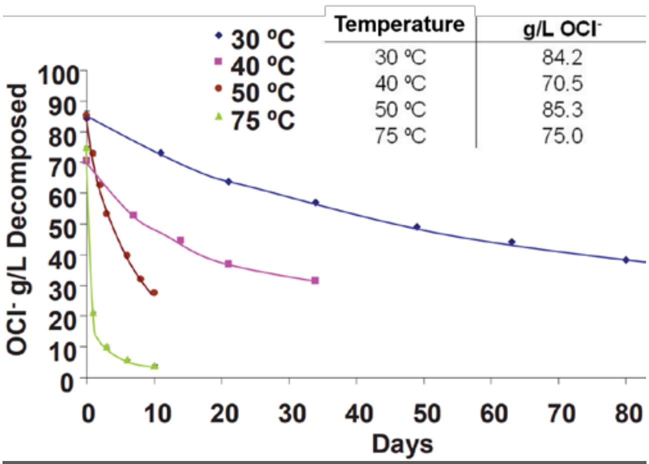

Figure 2: Decomposition of NaOCl at different temperatures

Importance of density/specific gravity

Density is a convenient analytical tool used in the chemical industry to quickly identify compounds and correlate product quality without the performance of time-intensive “wet chemistry” tests.

- Density measurements permit to quantify the concentration of NaOCl before and after dilutions facilitating the work of technicians
- Density can be used as quality parameter itself: the final customer only checks if the density matches with the value on the label
- Density is necessary parameter for conversion volume/weight

Furthermore, the drinking water providers purchase several chemicals such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) in order to operate a plant. The concentrations of all those chemicals can be easily determined by density measurements.

3 Determination of NaOCl concentration

As mentioned before, an improper use of NaOCl can lead to an ineffective disinfectant due to lack of active chlorine in case of low concentration or skin irritations in the opposite case.

The concentration of NaOCl should be checked during the delivery in order to avoid mistakes during the disinfection process and litigations with the suppliers.

The classical analytics used to determine the concentration of NaOCl is titration.

The titration process itself together with the cleaning of the instruments requires a lot of time, is prone to human error and needs qualified staff.

A determination of concentration by digital density is advisable.

The determination of the NaOCl density [12] permits to determine its concentration and calculate the %Active Chlorine for fresh samples as shown in following table 1.

Average Density	*% NaOCl*	*%Active Chlorine*	*Active Chlorine*
g/cm³	*w/w*	*w/w*	*g/L*
1.014	1.05	1.0	10.14
1.043	3.15	3.0	31.29
1.082	5.78	5.5	59.51
1.159	10.50	10.0	115.90
1.218	13.97	13.3	161.99
1.225	14.28	13.6	166.60

Table 1: Concentration determination of NaOCl by density at 20°C (table provided by Solvay)

4 DMA 35 for density measurements

DMA 35

The digital portable density meter DMA 35 can easily determine the density, and therefore the concentration of NaOCl and all liquid chemicals involved in the water treatment process with an accuracy of 0.001 g/cm³.

Density and temperature are measured simultaneously, and the instrument automatically performs the temperature correction.

2 mL of sample are filled into the instrument simply by pushing and releasing the pump button. Within a few seconds the result can be read from the large digital display, and stored in the memory.

Due to the automatic temperature correction, comparable results at e.g. 20 °C are quickly obtained, independent of the actual cell temperature. To obtain valid measurement results, the sample temperature has to be between 0 °C and 40 °C. After measuring DMA 35 can easily be cleaned with distilled water.

The analysis is carried out without any contact with chemicals reducing any risk of injury.

Figure 3: DMA 35 Portable Density Meter

Traditional density measurement

The traditional density measurement technique, pycnometry, requires skilled operators, large amounts of sample and cleaning agent, long analysis, cleaning times and needs a manual temperature correction.

5 Conclusions

Density measurement is a simple and convenient method to determine the concentration of fresh NaOCl (and calculate %Active Chlorine) and other chemicals such as HCl and H_2SO_4 (see application report E28IA004EN) used for water treatment.

DMA 35 is the perfect solution to check the concentration of NaOCl (and its dilutions) during the water treatment process within a few seconds avoiding a complex and slow analytical method such as titration, which requires skilled staff and is slow.

The concentration check of NaOCl avoids errors such as mislabeling and litigations with suppliers. Moreover, DMA 35 is a suitable solution during the process for chemical dilutions checks.

The device is portable, easy to handle (no training is needed) and reduces chemical exposure during the measurements.

6 References

[1]https://www.who.int/water_sanitation_health/dwq/S13.pdf

[2]https://www.who.int/water_sanitation_health/bathing/srwe2full.pdf

[3] https://www.who.int/ihr/publications/Annex7.pdf

[4]https://www.businessinsider.in/india/news/heres-how-sodium-hypochlorite-is-being-sprayed-on-the-streets-to-contain-the-spread-of-coronavirus/articleshow/74894017.cms

[5]https://www.epa.gov/rmp/amounts-chlorine-present-sodium-hypochlorite

[6]https://eur-ex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:325:0003:0065:EN:PDF

[7] Vogt H, Balej J, Bennett JE, Wintzer P, Sheikh SA, Gallone P (2007). "Chlorine Oxides and Chlorine Oxygen Acids". *Ullmann's Encyclopedia of Industrial Chemistry* (7th ed.). Wiley. p. 2

[8]https://echa.europa.eu/documents/10162/24380810/7494_1391-01_Assessment_Report.pdf/0f87765c-1bb2-9bb0-6b41-c8b54841dfd5

[9]https://www.oxy.com/OurBusinesses/Chemicals/Products/Documents/sodiumhypochlorite/bleach.pdf

[10]Hypochlorite ion decomposition, L.C Adam, G. Gordon Inorg. Chem. 1999, 38, 6, 1299–1304

[11]IOSR Journal of Applied Chemistry 7(1):19-23 January 2014

[12]http://www.sciencemadness.org/talk/files.php?pid=391303&aid=37353

Contact Anton Paar GmbH

Tel: +43 316 257-0
density@anton-paar.com
www.anton-paar.com