CHEMetrics, Inc.

October 2015

The Measurement of Dissolved Ozone

Ozone has become an important tool for the water quality engineer. As new more stringent requirements from regulators and customers must be met, ozone is often the oxidizer and disinfectant of choice for a wide range of process applications. These include viral, bacterial and parasitic disinfection, the removal of taste- and odor-causing compounds, the destruction of refractory/toxic organic matter and the coagulation or oxidation of inorganic impurities such as iron, manganese and sulfides[1].

With the rising popularity of ozone in water treatment comes the need for a versatile analytical method for routinely measuring dissolved ozone in a wide variety of solution matrices. The method must be accurate and precise over a wide concentration range, insensitive to interferences and easy to use and dispose of. The indigo trisulfonate method fulfills these requirements. It uses a non-toxic blue dye that is instantly decolorized by ozone. Interference from the most common oxidizer, chorine, can be masked with malonic acid. The method is described in Standard Methods for the Examination of Water and Wastewater (Method 4500-O3B)[2] and is offered as a product in various forms by a number of companies.

Drinking water public health standards have led to the expansion of ozone application for water treatment. The rules regarding the more resistant pathogens such as Cryptosporidium oocysts and some viruses, as well as the lowering of the allowable concentrations for disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs), are examples of such standards. In order for chlorine to be effective at disinfecting the more resistant pathogens, the concentration and/or contact time must be increased beyond what would otherwise be necessary. However this tends to increase THM and HAA concentrations. Therefore some utilities have installed ozone contactors to boost disinfection potential without the DBP production. Some conditions can limit the suitability of the ozone option. When bromide (Br^-) is present in the source water its oxidation by ozone can result in the production of bromate (BrO_3^-), a DBP with an EPA drinking water limit of 10 ppb[3].

Utilities that choose this ozone option tend to have greater customer satisfaction due to an improvement in other water quality parameters such as color, taste, odor and clarity. The ozone also removes dissolved inorganic impurities such as iron, manganese and sulfide by coagulation and oxidation more efficiently than a conventional aerator. This allows reduced coagulant dosage and contact time. Oxidation of refractory or toxic organic matter, such as humic acids and pesticides which may not be degradable by chlorine, biological oxidation, or ozone alone can often be enhanced by ozone supplemented with hydrogen peroxide or UV radiation. This is called Advanced Oxidation. The hydrogen peroxide or UV radiation rapidly degrades the ozone, releasing a pulse of extremely reactive free radicals.

Industrial and Commercial Applications of Ozone

New avenues for the application of ozone in the food industry were opened in 1997 when the U.S. Food and Drug Administration granted “generally recognized as safe” (GRAS) status to ozone. The cleaning of fruit and vegetables by washing and spraying with ozonated water decreases the concentration and volume of BOD waste, the total water consumption and the bacteria and mold contamination[4]. For meat, poultry and seafood, ozone can extend shelf-life and reduce processing costs. Generally, products are sprayed with ozonated water, and afterwards they can be kept in an ozonated atmosphere to further decrease spoilage and odor.

Bottled water production methods vary depending on the size of the operation and quality of the source water. However all methods for the U.S. market must produce a product that can pass the U.S. FDA regulations, which are required to be at least as protective of public health as those required by the EPA for public drinking water. Due to the use of filtration, reverse osmosis and activated carbon adsorption to remove natural and pollutant substances, and ozone treatment for disinfection, there had been no major outbreaks of illness associated with bottled water in the past decade in the United States[5].

In a bottled water plant, ozone is added to the water in the final operation just before the filling of the bottle. Generally ozone gas is injected into a large tank of water until it reaches a desired concentration after which the water is transferred to the bottle. The ozone concentration must be high enough to kill any organisms, yet low enough that it does not attack the bottle or linger long enough to greet the consumer. This is about 0.4 ppm (mg/L) ozone. [6] As with public drinking water, ozone may introduce the disinfectant byproduct bromate if the source water contains a significant amount of bromide.

Ozone is also applied as disinfectant and oxidizer in these applications: aquaculture (nitrite oxidation), pools and spas, soil/groundwater remediation (underground storage tank contaminants), farming, winery sanitation (barrel/tank cleaning), electronics (surface cleaning), cooling water towers, laundry (deodorizing), indoor air pollution (particle removal), and industrial wastewater in general.

Instrumental Methods of Analysis

The techniques for measuring dissolved ozone can be divided into two methods: instrumental and colorimetric. The three main instrumental methods are: 1) Oxidation/Reduction Potential (ORP), 2) membrane probe and 3) UV absorbance. These methods all offer the advantage of giving continuous readings, and they avoid ozone degassing during sampling when used in-line. The instruments are generally calibrated using colorimetric methods, except for the UV absorbance method.

1) Oxidation/Reduction Potential

The ORP method measures the voltage generated by the ozone in the solution at a platinum electrode relative to a standard reference electrode. It requires very clean water with at most moderate turbidity.

2) Membrane Probe

The membrane probe is similar to the ORP method but it has a gas permeable membrane over the platinum electrode. The ozone must diffuse through the membrane to reach the platinum electrode where it generates a voltage. The membrane probe can be used in fairly dirty water, but the membrane may need frequent replacement or cleaning.

3) UV Absorbance

Ozone has an absorbance peak in water at about 258 nm, which is in the UV region of the spectrum. The UV absorbance measurement method is commonly used for gas analysis but it may also be applied to clean water free of UV absorbing impurities.

Colorimetric Methods of Analysis

The three main colorimetric methods of measuring ozone in water are: 1) iodometric titration, 2) N, N-**d**iethyl-p-**p**henylene**d**iamine (DPD) and 3) indigo trisulfonate.

1) Iodometric Titration

In the iodometric method, ozone reacts with potassium iodide (KI) to form iodine (I_2), which is then titrated with thiosulfate to a starch indicator endpoint with the sample buffered to pH 2. However, the stoichiometry of the reaction is sensitive to pH, buffer composition, buffer concentration, iodide ion concentration, sampling techniques, and reaction time[7].

2) DPD

In the DPD method, ozone reacts with potassium iodide to form iodine which then reacts with DPD to produce a pink compound. The intensity of the pink compound is proportional to the ozone concentration. The intensity is measured at about 515 nm on a colorimeter or spectrophotometer. Iodometric and DPD methods have the disadvantage that they cannot discriminate between ozone and other common oxidizers. Several vendors manufacture colorimetric test kits that utilize DPD/KI in either powder or tablet form. However, the sample manipulation required to dissolve the tablet or powder can cause a loss in measured ozone concentration. This drawback is minimized by an ozone test kit with a liquid KI reagent that is added to the sample with a dropper bottle. This method, manufactured only by CHEMetrics, Inc., also uses a liquid DPD reagent packaged in a unit-dose glass ampoule sealed under vacuum. The reaction takes place inside the ampoule which increases the overall accuracy and precision of the method. The method is applicable to samples that do not contain chlorine.

3) Indigo Trisulfonate

The indigo trisulfonate method has several advantages over the other two techniques. According to Standard Methods, “The indigo colorimetric method is quantitative, selective and simple. The method is applicable to lake water, river infiltrate, manganese-containing groundwaters, extremely hard groundwaters, and even biologically treated domestic wastewaters.” Indigo trisulfonate is usually sold as the potassium salt. The purity of indigo trisulfonate may vary between vendors and even between different lots from the same vendor. Both purity and age of the indigo trisulfonate have been shown to affect the stoichiometry of the reaction with ozone[8]. High purity indigo trisulfonate (>80%) has a molar absorptivity of about 20000 $M^{-1}cm^{-1}$ at 600 nm.

The method is based on the decolorization of the dye by ozone, where the loss of color is directly proportional to the ozone concentration. The sample is generally adjusted to near pH 2 to minimize destruction of the ozone by reaction with hydroxide ions. The most common analytical procedure subtracts the absorbance of indigo trisulfonate after reaction with a sample from that of an ozone free blank. Chlorine decolorizes indigo trisulfonate at a moderate rate, but this can be significantly slowed by the addition of malonic acid.

Oxidation products from the reaction of the manganous ion (Mn^{+2}) with ozone can destroy indigo trisulfonate. In order to measure ozone in the presence of manganous ion, first glycine is added to a sample to selectively destroy the ozone, then indigo trisulfonate is added to measure the apparent ozone concentration due to the reaction with manganous ion oxidation products. This value is subtracted from the value obtained from a sample without glycine added.

Indigo Trisulfonate Test

Two of the major manufacturers of the indigo trisulfonate test are CHEMetrics, Inc. and the Hach Company. Both offer kits that include self-filling reagent ampoules. The active ingredients of both products are potassium indigo trisulfonate and malonic acid. The malonic acid in the CHEMetrics reagent prevents interference from up to 10 ppm chlorine. Hach does not publish a chlorine interference limit. In the Hach ampoule the indigo dye is dried on the surface of the ampoule and malonic acid is in powder form. CHEMetrics' ampoules contain a liquid reagent, advantageously allowing the dissolved indigo trisulfonate to instantly react with the ozone in the sample as it is drawn into the ampoule. This avoids the problem of ozone loss through side reactions while indigo trisulfonate and powder are dissolving.

Hach offers products in a variety of ozone concentration ranges: 0.01-0.25 ppm, 0.01-0.75 ppm and 0.01-1.5 ppm ozone. The ampoules are one inch (25.4 mm) in diameter and designed for use in Hach instruments. CHEMetrics' indigo ozone product offers a product with a single ozone concentration range of 0-0.75 ppm. The ampoules have a 13 mm diameter and are compatible with most spectrophotometers.

Since the ozone concentration is measured by the loss of indigo trisulfonate, both initial and final absorbance measurements are required. To accomplish this, the Hach products require measuring one ampoule in ozone free water (the initial indigo trisulfonate absorbance) and one in the sample (the final indigo trisulfonate absorbance). The difference in absorbance is converted to ozone concentration. The ampoule used to measure the initial indigo trisulfonate absorbance can be reused with a series of sample ampoules. The CHEMetrics product avoids the need for two ampoules by using a "self-zeroing" method that measures the absorbance of the same ampoule before and after sampling, eliminating the need to generate an initial indigo trisulfonate absorbance ampoule each time a test is run. The initial absorbance measurement, before taking in the sample, is divided by a factor that takes into account the dilution once the ampoule has filled. The difference between the initial absorbance divided by the factor, and the absorbance after sampling, is converted to ozone concentration. A direct read colorimeter, called a Single Analyte Meter, is available that automatically makes all appropriate calculations. Using a single ampoule per test makes the CHEMetrics method more efficient and less expensive than the Hach method.

References

1. Rakness, K., (2005) *Ozone in Drinking Water Treatment: Process Design, Operation, and Optimization.* AWWA.
2. Standard Methods for the Examination of Water and Wastewater, 22nd ed. (2012) 4500-03 B, 4-145 .
3. Haag, W. R., and J. Hoigne (1983) Ozonation of bromide-containing waters: kinetics of formation of hyprobromous acid and bromate. Environ. Sci. Technol. V17, p 261.
4. Spartan Environmental Technologies, LLC, Tech. Bulletin TA-112064.
5. Edberg, S., Microbial Health Risks of Regulated Drinking Waters in the United States: A Comparative Microbial Safety Assessment of Public Water Supplies and Bottled Drinking Water (2013) Drinking Water Research Foundation, 31 p.
6. Bollyky, L. J., Benefits of Ozone Treatment for Bottled Water (2001) http://pacificozone.com/wp-content/uploads/2014/04/app_1388591099.pdf.
7. Langlais, B., D.A. Reckhow, and D.R. Brink eds. (1991) Ozone in Water Treatment: Application and Engineering. Chelsea, Mich.: Lewis Publishers, Inc.
8. Gordon, G., R. Gauw, Y. Miyahra, B. Walters, and B. Bubnis (2000) Using Indigo Absorbance to Calculate the Indigo Sensitivity Coefficient. Jour. AWWA, V92, pp. 96-100.