



Application report

Concentration of Free Chlorine, Chlorine Dioxide [ClO₂] and Ozone [O₃] in Water

In the treatment of water (drinking water and process water), different methods are used for disinfecting water: UV disinfection, chlorine, chlorine dioxide or ozone are those best known. Seen on a global scale, chlorine is the most widely used. This refers to active or free chlorine.

Benefits

The measurement of the disinfectant ensures that the legal requirements are fulfilled.

Measurement of free chlorine (HClO)

This disinfectant is added to the water as a liquid. Depending on the water, concentrations of 10–30 mg/l are used. The liquid can be added at one or at several points in the treatment process. There are very different concepts.

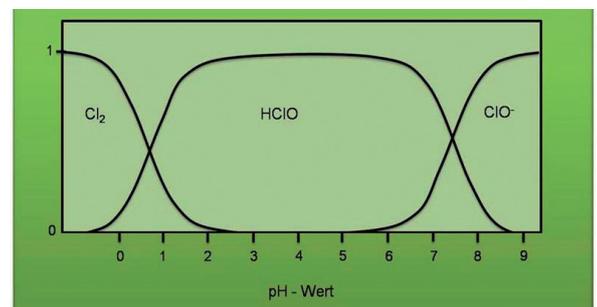
In order to measure the concentration of «free chlorine» on-line, there are various measuring principles:

- photometric measurement (DPD)
- amperometric measurement
- potentiostatic measurement

In many countries, photometric measurement is used as reference measurement. For this, reagents are needed, which results in operation costs depending on the desired measuring cycle.

For amperometric and potentiostatic measurements, no reagents are needed. In order to fulfil legal requirement, however, they have to be verified with the reference method at regular intervals and recalibrated if need be. How often this verification has to be carried out depends on the degree of soiling of the measured water and on the quality requirements of the end user.

Amperometric and potentiostatic measurements can only be used in the pH range of 6–8. In addition, the measurement of the chlorine concentration is dependent on the pH value itself. It has to be determined whether the pH value of the water is stable at the measuring point. Variations of the pH value of 0.1 pH units cause a measurement inaccuracy of the chlorine concentration of about 3–5% of the measuring range selected. As a result, some manufacturers offer measuring instruments with and without pH compensation.



Pict. 1: State of chlorine in the pH range 0–9

Measurement of chlorine dioxide (ClO₂)

This disinfectant cannot be purchased on the market as such. It is produced in a reactor at the site itself. A portion of the water is fed from the water main to the reactor. With this water, a high concentration (some grams/litre) of chlorine dioxide is produced. The water thus treated is fed back to the main pipe and a device is used to mix the chlorine dioxide with the rest of the water.

High concentrations of chlorine dioxide at the outlet of the reactor can be measured optically with a photometer (ColorPlus In-line).

Low concentrations of chlorine dioxide in water can also be determined on-line. In that case, three measuring principle are used.

- photometric measurement (DPD)
- amperometric measurement
- potentiostatic measurement

Measurement of ozone (O₃)

This disinfectant cannot be purchased on the market as such, either. It is produced with a generator at the site itself. A gas mixture of air/oxygen & ozone is fed to the reaction chamber in a pipe. Since ozone is an environmentally hazardous gas, it must be kept in a closed space. In some disin-

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fection plants, the waste air from the reaction chamber is fed to a residual ozone decomposer.

In such plants, the ozone concentration can be measured with a photometer (ColorPlus O₃ Gas) at the following two points:

- for high ozone concentrations: in the pipe connecting the generator and the reaction chamber
- for very low ozone concentrations: after the residual ozone decomposer as a proof that no ozone is left in the air.

However, ozone can also be detected in water on-line. In this case, the following three measuring principle can be applied:

- photometric measurement (DPD)
- amperometric measurement
- potentiostatic measurement

Measurement of hydrogen peroxide (H₂O₂)

This disinfectant is rarely used in the treatment of water itself. However, it is used for disinfecting objects, fruit, vegetables, fish, etc. For that reason, it can be found in water. In some applications, H₂O₂ itself or the absence of H₂O₂ has to be proven.

Typical application

As a rule, the concentration of a disinfectant is measured at the end of the water treatment process.

In many countries, a certain amount of disinfectant still has to be contained at that point to ensure that a reaction is possible during the transport through the pipes until the water reaches the consumer (protection of water networks). If free chlorine is used, concentrations of 0–1 mg/l are common at this point.

Cross-sensitivity

The potentiostatic measurement as offered by SIGRIST is cross-sensitive. That means that different disinfectants interfere with each other.

It has to be ascertained in any case that different disinfectants are not present in the same water.

SIGRIST product and configurations:

• AquaDMS without pH compensation

System for measuring the concentration of free chlorine, chlorine dioxide or ozone in pH-stable water (approx. +/- pH 0.1).

(The pH dependency only applies to the measurement of free chlorine)

• AquaDMS with pH compensation

System for measuring the concentration of free chlorine, chlorine dioxide or ozone with pH compensation.

(The pH dependency only applies to the measurement of free chlorine)

• Radon DES-pH laboratory photometer

Complete set for determining the concentration of the disinfectant according to the reference method EN ISO 7393-2.

Advantages of SIGRIST AquaDMS

- It is a ready-to-mount system with various sensors.
- The potentiostatic measurement does not have a zero drift.
- Stabilized flow at minimal water flow of 35 l/hour
- Optionally available: Complete set for determining (laboratory) the concentration of the disinfectant in accordance with the reference method EN ISO 7393-2.



All disinfectant sensors are equipped with the automatic sensor cleaning ASR®

- Cleaning interval can be selected
- No manual cleaning
- No chemical detergent is necessary
- Removes deposits of lime, grease and manganese dioxide



SIGRIST
PROCESS-PHOTOMETER

SIGRIST-PHOTOMETER AG
Hofurlistrasse 1 · CH-6373 Ennetbürgen
Tel. +41 41 624 54 54 · Fax +41 41 624 54 55
www.photometer.com · info@photometer.com