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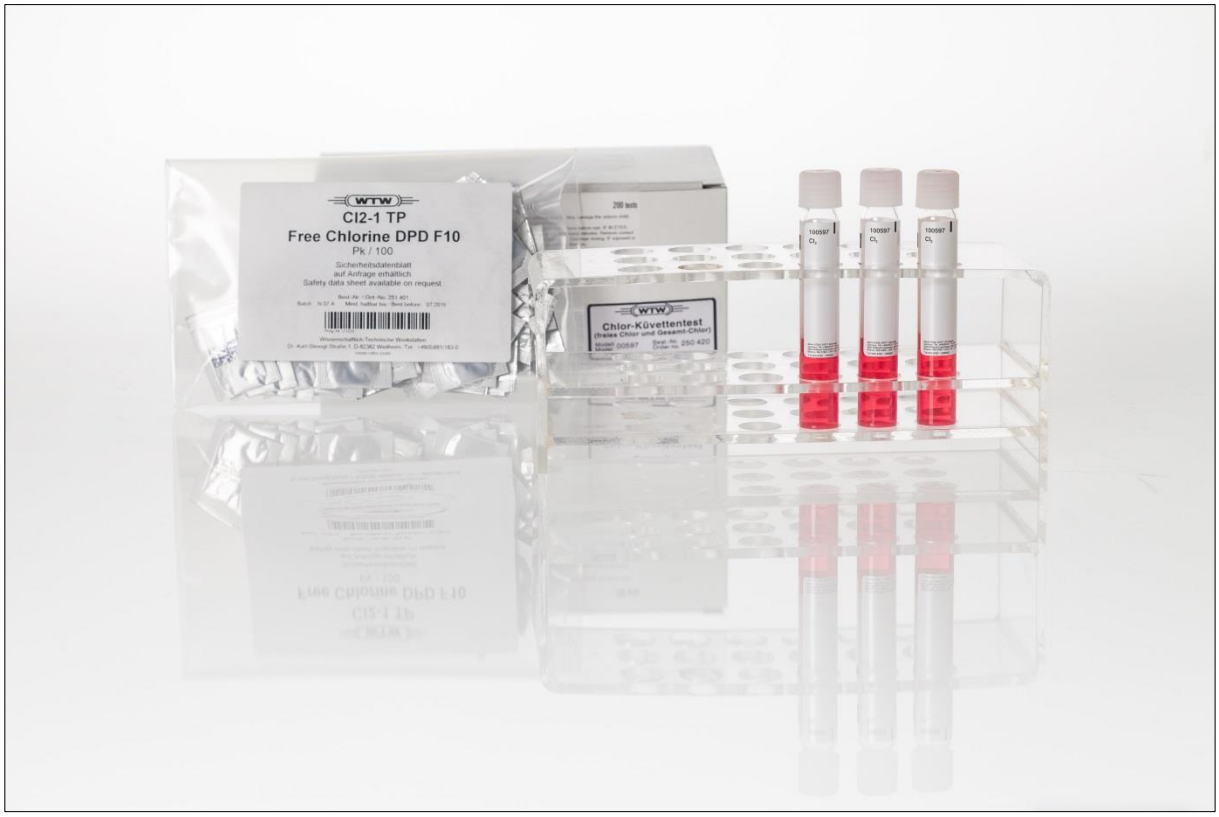


Chlorine – disinfectant in the water industry

Based on its chemical characteristics and its reactivity response, chlorine is very well suited for disinfection of water and to prevent contamination with bacteria and pathogens. Chlorine introduced into water exists in a pH-dependent balance; with a neutral pH level foremost as a Hypochlorous acid (HClO):

$Cl_2 + H_2O \rightarrow HClO + HCl$

Hypochlorous acid is a strong oxidizing agent: Its disinfecting effect consists of the irreversible clumping of protein of viruses and bacteria - similar to the effect of heat exposure.

With an increasing pH value, the balance in the water is shifted to the hypochlorite, which lowers the disinfecting effect:

$HClO + H_2O \rightarrow ClO^- + H_3O^+$

The regulation of the disinfection, of the agents used and the desired effect is discussed in national ordinances, as well as in superior organs such as WHO or the EU and the respective directives are constantly adapted.

Susanne Gollor, November 2017

Chlorine is added as chlorine gas, chlorine compounds, such as sodium hypochlorite or chlorine dioxide and is used

- *for emergency chlorination and transport chlorination* for broken pipes and contamination by germs in water protection areas, in wells, in the groundwater or during flood impact as well as for the protection from contamination in pipes. In the framework of the German drinking water ordinance 2001 (TrinkwV 2001) with the supplements added up until today, adding a max. of 1.2 mg/l free chlorine is permitted. After the completion of the mixture, no more than 0.3 mg/l of free chlorine must remain in the water. Areas with (temporary) exceptions could be e.g. flood zones.
- *for the standard disinfection during drinking water production* (in some countries; not in Germany).
- *for the disinfection in pools and of basin water*

The measurement of chlorine is also a deciding parameter for quality monitoring of drinking water as well as pool and basin water. In the wastewater industry, only sporadic measurements are conducted, e.g. during interferences, such as the inflow of chlorinated water from pools.

§ 11 of the TrinkwV 2001, Section Ic regulates the list of processing substances and disinfection-procedures, including limit values and approved chlorination substances.

The water treatment of pool and basin water is defined in the standard DIN 19643. The chemistry of disinfection with chlorine and side products that can be created in pool and basin water is very complex. The typical pool odor is mostly not caused by chlorine but by the reaction of the chlorine with the urea that enters the water through human skin and urine which turns them into nitrogenous chloramines such as monochloramine. The conversion products are combined as so called bound chlorine. Therefore, basin water have different limit values than drinking water. They are - as also published in the Federal Health Bulletin of 2014 by the Public Health Department - at .,3–0.6 mg/l free chlorine. For bound chlorine, this value is at 0.2 mg/l.

pH value and redox: Important indicators for the disinfection effect

The measurement of chlorine is accompanied by the measurement of the pH value and often with the redox voltage. The pH value is an indicator for the disinfection measurement: Due to possible pH shifts into the basic range because of the contamination of the basin water, in exceptional cases, concentrations of up to 1.2 mg/l free chlorine are permitted, as the chemical balance $HClO/ClO^-$ shifts from Hypochlorous acid to hypochlorite, which lowers the disinfecting effect.

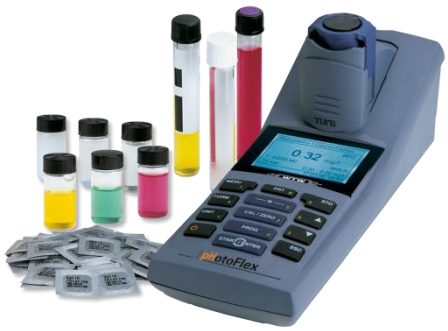
The measurement of the redox value is an indicator of the ratio between oxidizing to reducing substances, such as the contamination of the basin water. Thus, this provides information regarding the disinfection capacity of the chlorinated water: If the redox voltage is lower, there are more reducing substances and they may require a higher chlorine volume for the disinfection compared to water with a higher redox voltage. On the other hand, the lower value of the chlorine concentration of 0.2 mg/l depending on the (high) redox voltage may be permitted.

Turbidity particles: Source of contamination

Especially during flood or in swimming lakes, another important indicator parameter is added for disinfection: turbidity. Turbidity particles are a great settlement location for microorganisms. Turbidity itself is also an indicator of an increased risk for microbial contamination. The Drinking Water Ordinance lists an upper limit values of 1 FNU (Formazine Nephelometric Unit) or 1 NTU (Nephelometric Turbidity Unit).

A "real" multi-parameter device for monitoring

In addition to self-monitoring by communal water suppliers, operators of thermal baths and pools and similar operators in the water industry, especially health departments are busy in this sensible area: From emergency inspections related to introducing measures to regular monitoring.



Many health departments and water suppliers as well as service labs therefore use several pHotoFlex® Turb for the mobile monitoring of drinking water systems, wells, community pools or thermal baths. This portable photometer has all necessary programs for photometric water inspections to the smallest of measuring ranges by means of the flexible cuvette system of 16 and 28 mm cuvettes as well as the standardized colorizing measurement at 436 nm in (drinking) water.

Being a true multi-parameter device, it covers the important parameters pH, redox voltage and turbidity in addition to the photometric measurements as well as chlorine concentration: The measurement of pH and redox voltage is conducted via classic electrochemical sensors with calibration protocols. The important nephelometric turbidity measurement by means of infrared light allows a measurement to the lowest measuring range - as per standard and suitable for drinking water with lab quality with adjustable calibration interval and documentation.

Chlorine test kits - a tough choice

The bandwidth of the chlorine test kits for bound and free chlorine, total chlorine and monochloramine is huge. How does a user find his way through this thicket?

The price is not always the only criterion. And frequently, the expensive cuvette test with analytical quality assurance and bar code is even cheaper and more cost-efficient than the seemingly reasonable test. Therefore, the following requirements should be considered during the selection process:

- Is analytical quality control (AQS) desired?
- What is the required lower limit of the measuring range?
- Will the measurements take place in the lab or in the field?
- How often will measurements be conducted?

Susanne Gollor, November 2017

- Is there high humidity or strong wind in the measurement environment?
- Is there a large pH window during the test execution?
- What is the total cost?

For health departments, there will be a pre-selection of tests with batch certificates due to the desire for AQS. If series inspections are conducted, there is a lot of routine: Here, the price to performance ratio for test kits in the 10, 20 and 50 mm rectangular cuvettes is extremely good. Also, these test kits cover a large measuring range up to the trace analysis. The ones who measure less, appreciate the uncomplicated handling with the highest possible comfort. For the selection of the measuring system, the site of use can be a deciding factor: Will you measure a lot in the field or will the lab conditions be available on the road as well? Test kits, such as the small packaged single portions with powder kits are very cost-effective practical in a dry and wind-protected environment. Here are the details of the different test types:

- **Round cuvette tests with batch certificate** are mostly one thing: super comfortable and easy to handle. Depending on the test, a combined determination of free and total chlorine. Round cuvette tests are packaged as a set with cuvettes and powder reagent. Pipette the sample directly, add reagent, measure.

  If you use the universally usable pHotoFlex® Turb in the lab with its "lab station", you can also utilize the bar code of the test kits via an external bar code reader for the retrieval of the respective program. As a special feature, the round cuvette test 00597 for free and total chlorine can also be used in the 28 mm cuvette. Therefore a measuring range starting from 0.025 mg/l for mobile measurement can be provided.

- **Rectangular cuvette test with batch certificate:** For the largest "family package", the price per determination is sensationally low at a little more than 10 cents! And they are not much more difficult to handle than the round cuvette tests: Only the refilling into the rectangular cuvettes from the supplied round cuvette, but the test allows the lowest measuring ranges!

- The "**drop test"** is becoming more and more popular in practice with pHotoFlex® Turb with its test sets 00086–00088: The single reagents, depending on the combination, allow the determination of free and total chlorine in one step by consecutive drop adding of the different added reagents.

  The great strength of this test type is the handling in high-humidity environments. Here, there will not be any clumped reagents! This is also very well-suited for thermal baths, swimming and recreational pools as well as for the monitoring health departments. And, in outdoor applications, this test is the most "streamlined": no blow off of the reagents, but simple addition of drops into the supplied round cuvette.

- **Powder tests**, so-called powder pillows: What is practical here, are the single portions that are added to the measuring cuvette, which can be well-planned for use on the road. Thus, reagents will not be exposed to unnecessarily high transport and ambient temperatures. Regarding the price per determination, powder tests almost always offer the most favorable solution. Perhaps, the pH must be adapted and dilution water may have to be used, which requires are more accurate handling compared to cuvette tests with their additional pH windows.

Susanne Gollor, November 2017

Conclusion: Chlorine measurement is a very important measurement and it rarely occurs alone

Water is susceptible to impurities and contamination with pathogenic germs. Chlorine is still the most important disinfectant for basin water and drinking water in the areas of emergency or transport chlorination. In some countries, chlorine is used by default obligatorily for the treatment of drinking water.

Therefore, a respective amount of choices of solutions is available for chlorine measurements. Especially for monitoring, a universal and easily transportable device, such as the portable photometer photoFlex® Turb bears an advantage, which can also record and document the important indicator parameters pH, redox voltage and turbidity in a standardized manner. Analytical quality assurance and the ease of handling are foremost factors in the selection of suitable test kits, depending on the usage site.

Susanne Gollor, November 2017