Information on the amperometric measurement of free chlorine, chlorine dioxide and ozone in water

Dr. Jürgen Schleicher

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Note
This reference work has been created to the best knowledge and belief. We assume no liability for possible errors. The definitive source of information is always the operating manual for the relevant device.

Preface

For reasons of hygiene, drinking water, or any other water that people come into direct or indirect contact with, often has to be treated with compounds that destroy any micro-organisms contained in it. Chlorine, chlorine compounds or ozone are very often used as disinfectants. In this sensitive area, a high level of safety for the consumer is an absolute requirement, and for this reason, systems are used for fully automatic monitoring, control and recording of the disinfectant concentration.

Amperometric sensors provide the best means of monitoring the disinfectant concentration. This technical publication will present the electrochemical fundamentals and the application technology of such sensors in an easily understood form, for the interested reader.

We are trying to keep this “Information on the amperometric measurement of chlorine, chlorine dioxide and ozone in water” fully up to date. In case of doubt, please consult the current legal requirements and appropriate standards. We call upon our readers to take part in an active exchange of experience and knowledge. Your suggestions and contributions to the discussion would be most welcome.

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1 Introduction

Water is our most important food: without sufficient water ingestion, a person can only exist for a short time. Many of our other foods and foodstuffs contain water to a large extent too, are mixed with water, or come into contact with water during their preparation. Hence, it is an existential issue for mankind to have water available in sufficient quantity, and of good chemical and microbiological quality.

Our drinking water is usually obtained from groundwater or surface water and reaches the consumer via mainly local networks. Depending on the existing water quality, various chemical, physical and microbiological steps must be sequentially arranged until a quality is reached that can be made available to the consumer via the distribution system.

The hygienic quality of the water is of special importance here: whereas with chemical impurities a certain minimum concentration must be present for a biological effect to occur, even a few pathogens in the water can be enough to cause various serious diseases. Under favorable growth conditions and with an adequate supply of nutrients, the pathogens even multiply in the distribution system. Epidemics occur in many developing countries as a result of pathogens in the water. As recently as 1919 and 1926, several hundred people died in Pforzheim and Hannover during typhoid epidemics. One of the most fundamental advances in public health in the 20th century owes much to the hygienic treatment of drinking water.

Not only the water that is ingested directly by people, but also the water that comes into contact with people in any way, must be of a perfect hygienic quality. This also involves, for example, bathing water in swimming baths and water used for washing or rinsing in food processing plants.

1 Introduction

2.1 Regulations for hygienic water quality

The hygienic requirements that are set for water are laid down in various laws and regulations:

Drinking water
“Drinking water must be free from pathogens” (Drinking Water Regulations)
Drinking water and water for food processing must be of such a quality that its use or consumption should not give rise to concern about damage to a person’s health, particularly as a result of pathogens” (§ 11 of the German Federal Law concerning Epidemics).

Bathing water
“Swimming or bathing pool water in public baths or commercial enterprises must be of such quality that its use should not give rise to concern about damage to a person’s health due to pathogens. In this respect, swimming pools or bathing pools, including their water treatment plants, are subject to monitoring by the public health department” (§ 11 of the Federal Law concerning Epidemics).

2.2 Permitted disinfectants for drinking and bathing water

Permissible disinfectants for drinking water
in accordance with the Drinking Water Regulations (Appendix 3) are:

- chlorine (gas) (Cl_2)
- sodium hypochlorite ($NaOCl$), calcium hypochlorite ($Ca(OCl)_2$),
  magnesium hypochlorite ($Mg(OCl)_2$) or chlorinated lime ($CaCl(OCl)$)
- chlorine dioxide (ClO_2)
- ozone (O_3)

Permissible disinfectants for bathing water
in accordance with DIN 19643-1 (Treatment of swimming and bathing pool water) are:

- chlorine (gas) (Cl_2)
- sodium hypochlorite ($NaOCl$)
- calciumhypochlorite ($Ca(OCl)_2$)

Basically
the disinfectants used for the disinfection of water are all oxidizing agents.

2.3 Treatment of water with oxidizing agents

Disinfection/sterilization
The treatment of water serves primarily to destroy or reduce the micro-organisms (bacteria, viruses etc.) contained in it. This process is also referred to as disinfection or sterilization. The primary function of inactivating the pathogenic micro-organisms (pathogens) is supplemented by additional effects of the oxidizing agent to further improve quality:

- oxidation of Fe (II+) and Mn (II+) to Fe (III+) and Mn (IV+), which precipitate as iron hydroxide and manganese oxide, and hence can be removed.
- any deterioration in the microbiological quality of the water en route to the consumer is avoided by the presence of a residual disinfectant content.
- elimination of unwanted odors and tastes by oxidation.
- improved effectiveness of coagulation and filtration processes (removal of foreign substances).
- removal of discolorations of the water that can be caused by humic substances, for example.
- prevention of the growth of algae, for example, in filters and sedimentation tanks.

By-products
When treating water, every effort must be made to ensure that as few as possible unwanted by-products, such as trihalomethanes, for instance, are produced during the disinfection. This can be controlled to some extent by the conditions (chlorine quantity, temperature, pH value, etc.) under which the disinfection occurs. In addition, the precursors of unwanted by-products in the water that would react with chlorine can be removed by a pretreatment with ozone.

2.4 Criteria for hygienic water quality

Direct proof that **drinking water** does not contain any pathogens (pathogenic germs) cannot be produced as a a matter of routine. Limit values and standard values for indicators have been laid down, which indicate the possible presence of pathogens. Examples of indicator bacteria are Escherichia coli (E.coli), coliform bacteria and fecal streptococci, which should not be contained in a test quantity of 100 ml water (§ 1 Section 1 of the Drinking Water Regulations).

In addition, an upper limit is laid down for the sum of all bacteria contained: “In drinking water, the colony count must not exceed the standard value of 100 per ml at an incubation temperature of 20 ± 2 °C and at an incubation temperature of 36 ± 1 °C.” (§ 1 Section 2 of the Drinking Water Regulations).

The colony count is an indicator for the purity of the water. Hence it is a parameter with which an improvement (lower count) or deterioration (higher count) in the microbiological quality can be detected.

The microbiological requirements for **bathing pool water** can be obtained from DIN 19 643, Part 1. The same limit values as for drinking water are applicable for the colony count; the bacteria Pseudomonas Aeruginosa, E.coli and Legionella pneumophila must not be detectable in a 100 ml sample of the pool water.

2.5 Chlorination of water

Standard
Chlorination is the most frequently used disinfection process for water. There are a number of methods of adding chlorine or appropriate compounds to the water (see chapter 2.2 *„Permitted disinfectants for drinking and bathing water“*). In practice, the usual procedure is firstly to prepare a solution of chlorine gas or hypochlorite in water, and then to dose the water to be treated with the required quantity of this solution. Suitable starting solutions can be prepared on site by electrolysis of aqueous sodium chloride solutions. The chlorine gas produced here then dissolves immediately in the water.

Chlorine gas
The bactericidal effect of chlorine gas (Cl_2) is based mainly on the hypochlorous acid (HClO) that is formed in water:

$$Cl_2 + H_2O \rightleftarrows \underset{\text{(hypochlorous acid)}}{HOCl} + \underset{\text{(hydrochloric acid)}}{HCl}$$

Chlorine gas (Cl_2) reacts with water (H_2O) to form hypochlorous acid (HOCl) and hydrochloric acid (HCl). As hydrochloric acid is a strong acid, it causes a reduction in the pH value, if there is no buffering action in the water. For this reason, the pH value must be adjusted to the desired value with lye, if need be. The above reaction is an equilibrium reaction. The state of equilibrium is pH and temperature dependent.

Hypochlorous acid
HOCl is a weak acid ($pK_a = 7.5$). At higher pH values, HOCl increasingly dissociates under the formation of hypochlorite ions ClO^-:

$$HOCl + OH^- \rightleftarrows H_2O + OCl^-$$

The hypochlorite ions also have a disinfecting effect, but to a much lesser extent than HOCl. Hence, waters with increased pH values have an increased chlorine requirement, and require a longer reaction time or higher reaction temperatures.

Hypochlorite
The use of hypochlorites, e.g. sodium hypochlorite (NaOCl), offers another possibility for the disinfection of water.

$$NaOCl + H_2O \rightleftarrows \underset{\text{(hypochlorous acid)}}{HOCl} + \underset{\text{(sodium hydroxide)}}{NaOH}$$

The sodium hydroxide produced in the reaction is a strong base, and in weakly buffered solutions can cause an increase in pH. This must be corrected to the right pH value by the addition of an acid, if need be.

Temperature and pH value dependence
Apart from the temperature dependence, the state of equilibrium between chlorine gas dissolved in water (Cl_2(aq.)), hypochlorous acid (HOCl) and hypochlorite (OCl^-) is mainly dependent on the pH value.

$$Cl_2(aq.) \rightleftarrows HOCl \rightleftarrows OCl^- \qquad \text{(pH-dependent equilibrium)}$$

The quantitative relationship
of HOCl and OCl^- is clarified by means of the following diagram:

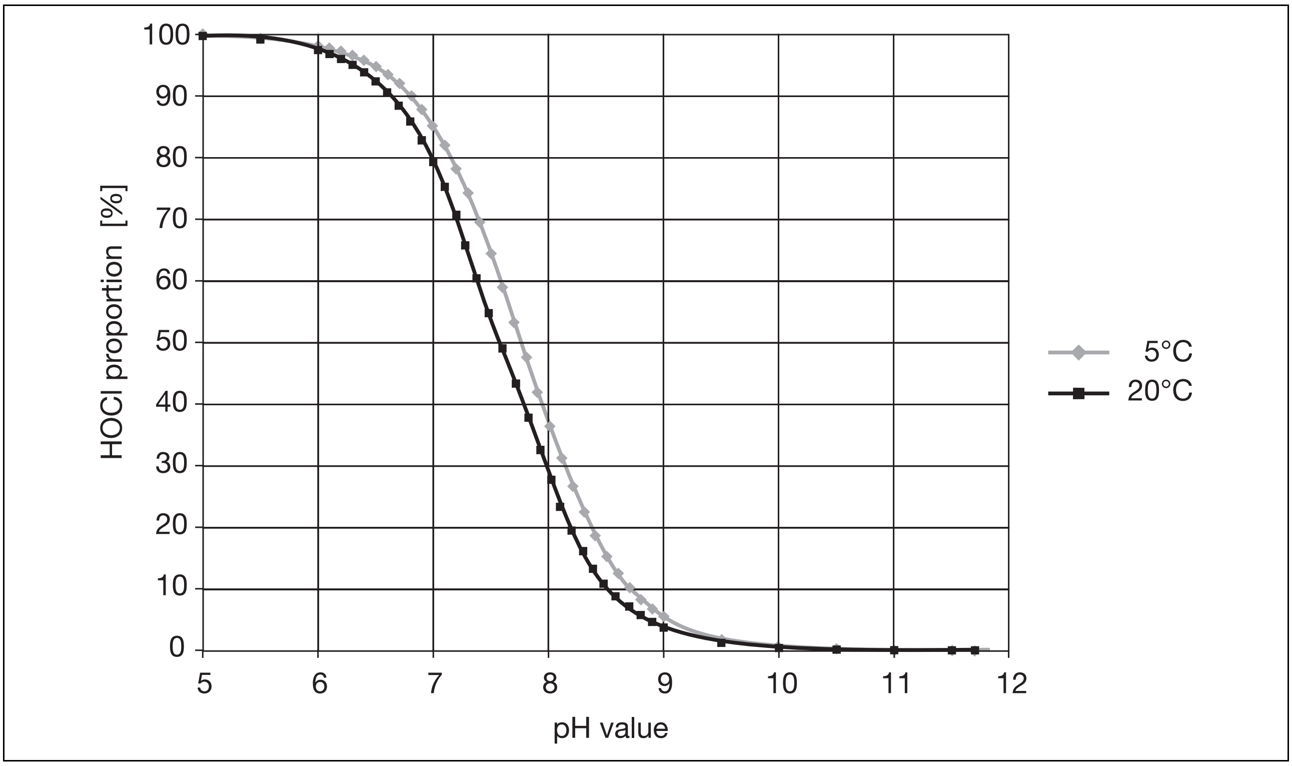

Fig. 1: Ranges of existence of hypochlorous acid and hypochlorite as a function of the pH value for 5°C and 20°C. The graph shows the percentage component of HOCl, the component of OCl^- is given by: 100-[HOCl].

From Fig. 1, the following points can be made about the individual pH ranges:

pH range	Predominant components	Example
3 – 6	HOCl	at 20°C HOCl > 95%
6 – 9	mixtures of HOCl and OCl^-	at pH 7 and 20°C ≈ 80% HOCl, ≈ 20% OCl^-
		at pH 8 and 20°C ≈ 28% HOCl, ≈ 72% OCl^-
> 9	OCl^-	at pH 9 and 20°C HOCl < 5%

In the lower pH range below 3, as well as HOCl, Cl_2 gas is also increasingly present, physically dissolved in the water but not yet dissociated.

Temperature dependence
The lower the temperature, the higher is the HOCL component, for a given pH value.

During the disinfection of water, the pH value must be adjusted and then maintained. At too high pH values, the rate at which bacteria are destroyed is greatly reduced, whereas at too low pH values there is a risk of corrosion.

Note
Fundamental pH limit values for drinking water:

- EU Directive concerning the quality of water intended for human consumption (80/778/EEC): Standard count = 6.5 to 8.5, Maximum permissible value = 9.5.
- WHO guideline value: < 8.0
- Appendix 4 of the Drinking Water Regulations: 6.5 – 9.5
  Additional remarks:
  a) with metallic or cement-containing materials, excluding passive steels, in the pH range 6.5 – 8.0, the pH value of the water supplied must not lie below the pH value of the calcium carbonate saturation.
  b) with fiber-cement materials, in the pH range 6.5 – 9.5, the pH value of the water supplied must not lie below the pH value of the calcium carbonate saturation.

The pH limit values for bathing pool water are laid down in DIN 19 643 (Treatment of swimming and bathing pool water). For bathing pool water, the generally applicable values are pH 6.5 - 7.6 (fresh water) and pH 6.5 - 7.8 (sea water) – please refer to the standard for special cases.

In practice
To ensure an effective disinfection during the addition of Cl_2 or NaOCl, a pH value is most likely set in the lower pH desired range. On the other hand, it should be noted that increased corrosion of metal, concrete etc. occurs in the acid region. Because of this, a compromise is necessary, and a pH value in the approximate range of 7.2 to 7.4 is set in practice.

2.5.1 Definitions

Indices
In accordance with EN ISO 7393-2 (formerly DIN 38408-G4), the following indices are distinguished for the concentration of chlorine in water:

- free chlorine:
  Cl_2 (aq.), HOCl, OCl^- (according to the pH value present).
- combined chlorine: chloramines (NH_2Cl, $NHCl_2$, NCl_3 and organic chloramines e.g. CH_3NHCl).
- total chlorine: sum of the free and combined chlorine.

Dosing
The chlorine content in water that was dosed with chlorine or hypochlorites is expressed as free chlorine in mg/l Cl_2.

Drinking water
Depending on the quality of the untreated water, up to 1.2 mg/l Cl_2 may be added to drinking water. When the treatment is complete, the concentration of free chlorine must not exceed 0.3 mg/l (Appendix 3 of the Drinking Water Regulations). Trihalomethanes (THM: $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$) are permissible up to a maximum of 0.01 mg/l (Appendix 3 of the Drinking Water Regulations). According to the Drinking Water Regulations, when chlorine is used for disinfection, then the drinking water must have a residual concentration of 0.1 mg/l Cl_2 after the treatment (§ 1 Section 4 of the Drinking Water Regulations). In special cases, the Drinking Water Regulations allow the addition of up to 6 mg/l Cl_2.

Bathing pool water
In accordance with DIN 19 643 Part 1 (Treatment of swimming and bathing pool water), the following limit values for free chlorine are applicable here:
General: 0.3 - 0.6 mg/l Cl_2
Heated whirlpools: 0.7 - 1.0 mg/l Cl_2

Please observe the additional limitations in DIN 19 643!

DIN 19 643 Part 1 gives upper limit values of 0.2 mg/l and 0.02 mg/l for combined chlorine and trihalomethanes, calculated as chloroform.

2.6 Use of chlorine dioxide as a treatment method for water

Action
Chlorine dioxide (ClO_2) dissolves as a gas in water. No hydrolysis occurs here, in contrast to the case with chlorine. The disinfecting action of chlorine dioxide is based on an oxidation reaction of the unwanted substances contained in the water, during which the chlorine dioxide is reduced to chlorite (ClO_2^-).

Caution !
Because of its explosiveness, chlorine dioxide cannot be stored in compressed form or in highly concentrated solutions. For this reason, ClO_2 is produced on site, using sodium chlorite ($NaClO_2$) and chlorine (Cl_2) or sodium hypochlorite (NaClO), and from sodium chlorite and hydrochloric acid (HCl):

$$2\,NaClO_2 + Cl_2 \longrightarrow 2\,ClO_2 + 2\,NaCl$$

$$2\,NaClO_2 + HOCl \longrightarrow 2\,ClO_2 + NaCl + NaOH$$

$$5\,NaClO_2 + 4\,HCl \longrightarrow 4\,ClO_2 + 5\,NaCl + 2\,H_2O$$

Depending on the reaction conditions during the production of ClO_2, it is possible that chlorate (ClO_3^-) is formed as an unwanted side reaction.

Dosing
Chlorine dioxide may be added to the drinking water up to a concentration of 0.4 mg/l. When the treatment is complete, the concentration of chlorine dioxide must be between 0.05 and 0.2 mg/l (§ 1 Section 4 and Appendix 3 of the Drinking Water Regulations).

2.7 Use of ozone as a treatment mehtod for water

Action
Ozone is one of the strongest oxidizing agents available. It reacts very quickly with impurities in the water and hence renders them harmless. Ozone can dissociate in water in a complex mechanism to form free hydroxyl radicals. Free hydroxyl radicals are amongst the strongest oxidizing agents occurring in water. Oxidation of the substances contained in the water can occur either indirectly via the highly reactive hydroxyl radicals, or directly via ozone. Which oxidation mechanism occurs preferentially depends on the prevailing conditions (higher pH, presence of UV radiation -> favor hydroxyl radicals). Nevertheless, the oxidizing capability of ozone in water treatment is only slightly dependent on the pH value.

In addition to its actual disinfection task, ozone can also be used for:

- oxidation of inorganic substances including Fe (II+), Mn (II+) and sulfides.
- oxidation of organic contaminants including substances that change the color, smell or taste of the water, together with phenolic contaminants and pesticides.
- ozone treatment prior to a chlorination: reduction of the amount of chlorine required and a decrease in substances that would form troublesome by-products with chlorine.

Production
Ozone is produced directly in the area of use by electric discharge or by electrolytic means. Depending on the method, either air or oxygen is used.

Dosing
With ozone treatment, the Drinking Water Regulations allow the addition of max. 10 mg/l ozone. The upper limit after the treatment is 0.05 mg/l (Appendix 3 of the Drinking Water Regulations).

Because of its high reactivity, the ozone is usually consumed quickly. For this reason, with long pipeline routes, it may be necessary to protect the water against recontamination en route to the consumer, by the addition of chlorine, for example.

2.8 Advantages and disadvantages of chlorine, chlorine dioxide and ozone as treatment methods for water

2.8.1 Chlorine

Advantages
- well-tried, safe and economical disinfection method.
- inactivates a broad spectrum of pathogens present in water.
- residual concentration in water can be easily measured and controlled.
- Mn (II+), Fe (II+) and hydrogen sulfide are oxidized.

Disadvantages
- pH-dependent disinfecting action.
- formation of unwanted by-products is possible, e.g. trihalomethanes formation from fulvic and humic acid (→ dangerous to health, carcinogen?).
- chloramines formed in the presence of ammonia or amines
  (swimming pool → unpleasant odor, irritation of the eyes and mucous membranes, dangerous to health).
- chlorophenols formed, should the water contain phenols
  (→ adverse effect on smell and taste).
- high potential danger with uncontrolled discharge of chlorine gas.

2.8.2 Chlorine dioxide

Advantages
- disinfecting action not as strongly dependent on pH value as with chlorine.
- ClO_2 has stronger disinfection (oxidation) effect than chlorine.
- substances with unpleasant odors and tastes (e.g. phenols, algae...) in the water are oxidized (conversion to substances with neutral odor and taste).
- Mn (II+) and Fe (II+) are oxidized, even in complex form.
- ClO_2 is very stable in water. A surplus can be maintained for a long time after the initial consumption has ceased (avoidance of recontamination with long pipeline routes).
- ClO_2 does not form chloramines with ammonia.
- trihalomethanes are not formed, as the original compounds are oxidized. The formation of other halogen compounds can be avoided by precise
  control of the reaction conditions.

- no foul-smelling chlorophenols are formed with phenols.
- odor and taste limit is higher than with chlorine.

Disadvantages
- considerably more expensive than chlorination.
- chlorite and chlorate can be formed as unwanted by-products during the production of ClO_2.
- decomposition of ClO_2 due to sunlight.
- high potential danger with uncontrolled discharge of chlorine dioxide.

2.8.3 Ozone

Advantages
(see also chapter 2.7 *„Use of ozone as a treatment mehtod for water“*)

- strong disinfectant (stronger than Cl_2 and ClO_2), hence only short reaction time required.
- the biocidal action is independent of pH.
- oxidation of organic substances (e.g. humic substances) has the effect of improving the odor, taste and color of the water.
- when ozone decomposes, only soluble oxygen is formed (“non-residual”).
- ozone does not form any by-products containing halogens
  (exception: if Br^- ions are present in the water → formation of bromate ions, bromoform, brominated acetic acid etc.)

Disadvantages
- relatively high costs (plant, energy...).
- when air is used to produce O_3, the formation of oxides of nitrogen as unwanted by-products is possible (→ formation of organic nitrates).
- formation of unwanted by-products in the water is possible: aldehydes, ketones, carboxylic acids, bromate and brominated organic compounds in the presence of bromide ions.
- because of its high reactivity, the ozone breaks down relatively quickly. In view of this, a secondary disinfectant must be used to prevent a possible recontamination of the water or the formation of a biofilm in the distribution system.
- ozone is corrosive and highly toxic (danger with uncontrolled escape).

3.1 Determination of chlorine in accordance with EN ISO 7393-2 (formerly DIN 38408-G4)

The photometric determination
of chlorine with the DPD method (DPD = N,N-diethyl-p-phenylenediamine) is based on the following reaction equation:

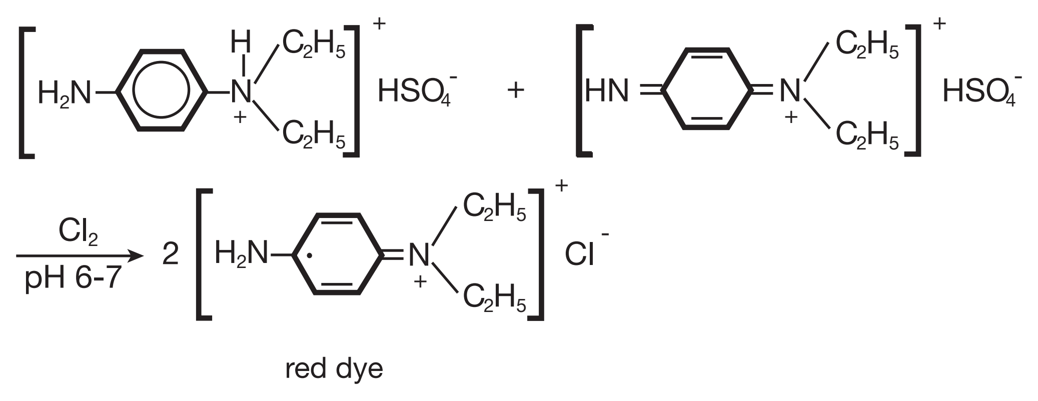

Fig. 2: Reaction equation for the reaction of DPD with chlorine (from L.A. Hütter, Wasser und Wasseruntersuchung, 6. Auflage, (Water and Water Testing, 6th edition) Verlag Salle Sauerländer, Frankfurt/M, 1994)

Method
The measured variable used here is the absorption peak of the UV/vis spectrum of the red dye that is formed by the reaction of DPD with Cl_2. The absorption is proportional to the available dye concentration and to the quantity of free chlorine present.

In the presence of iodide ions, only the free chlorine is measured. If potassium iodide is then added, the chlorine substitution products present in the sample release a stoichiometric amount of iodine which reacts with DPD according to the above equation, taking the place of the Cl_2. The result obtained is the total chlorine content. The difference of the total chlorine and the free chlorine gives the combined chlorine.

In addition to the DPD method there are also two further methods for the determination of chlorine: a titrimetric method using DPD as the indicator (EN ISO 7393-1), and an iodometric method (EN ISO 7393-3).

3.2 Determination of chlorine dioxide in accordance with DIN 38 408-G5

Titration
This method is based on the oxidation of DPD by ClO_2. The dye formed is then bleached by titration with ammonium iron (II) sulfate solution. The concentration of chlorine dioxide can be calculated from the amount of solution used.

Alternative
As an alternative to this method, a photometric determination of ClO_2 with DPD is also possible. As with chlorine, the concentration of the ClO_2 is calculated from the absorption, using a factor specific to chlorine dioxide.

3.3 Determination of ozone in accordance with DIN 38 408-G3

3 methods
Three methods for the determination of ozone are listed in this standard. An iodometric titration and two photometric determinations using DPD or indigo trisulfonate. Of these, the DPD method is probably the one most often used in the field of operational control. Ozone reacts with DPD to form a red dye, in the same way as chlorine and chlorine dioxide. The ozone concentration is calculated from the measured absorption using a factor specific to ozone.

3.4 Continuous measuring method for disinfectant concentration

Continuous measurement
The determination methods already described are **not** continuous (online) measuring methods, and samples are taken at specific times and individual measurements carried out.

DIN 19643 specifies a **continuous** measurement, control and recording of free chlorine and pH value for the treatment of swimming and bathing pool water (exception: cold water plunge pools $< 2\,m^3$).

For the control of the disinfectant concentration, it can be advantageous if an electrical signal proportional to the disinfectant concentration is permanently available. This signal can then be used as the input signal to a dosing plant for the disinfectant, i.e. the concentration can be completely automatically controlled.

3.5 Amperometric sensors

One possible method for the continuous determination of free chlorine, chlorine dioxide or ozone is the electrochemical determination using amperometric sensors.

Measuring principle
The substance to be determined (e.g. chlorine) reacts on the working electrode (cathode). A current is measured that is proportional to the concentration of that substance in the solution.

Versions
Amperometric sensors can be subdivided according to the following criteria (see Fig. 3):

- 2-electrode systems
- 3-electrode systems with potentiostatic switching

The sensors are available in both open and membrane-covered versions.

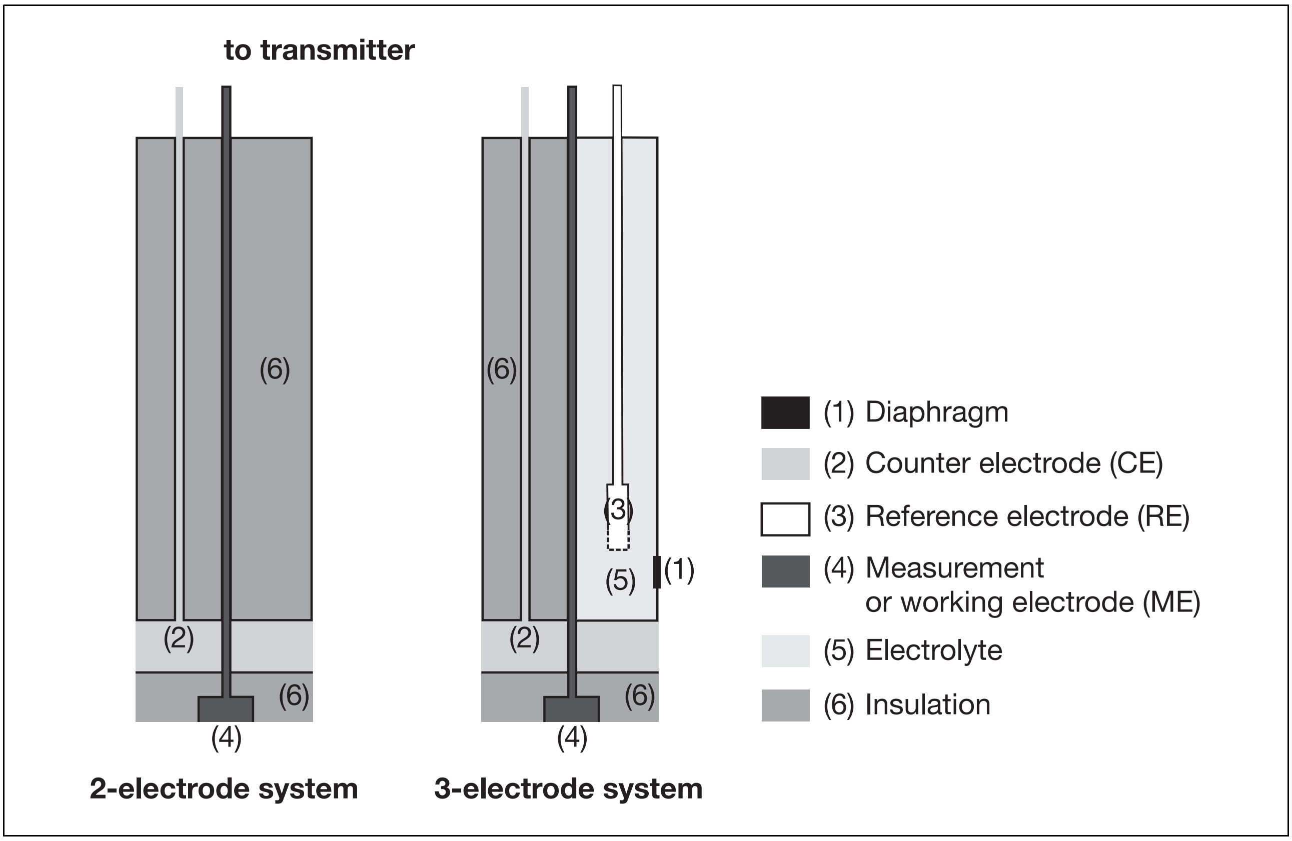

Fig. 3: Schematic representation of amperometric sensors showing 2-electrode and 3-electrode methods of construction

Direct contact
Where the water to be tested is in direct contact with the electrodes, an inactivation of the electrode is possible due to a build-up of dirt or an electrochemical side reaction. In this case, continuous cleaning of the electrodes using either quartz sand or glass or teflon beads is required. The water to be measured flows through a special flow-through fitting to ensure an adequate agitation of these cleaning particles. The constant contact of the particles with the surfaces of the electrodes keeps them free from contamination.

Protected electrodes
One possible way of keeping harmful contaminants away from the electrodes is to seal off the measuring cell with a microporous membrane (see Fig. 4). In this way, the electrode chamber filled with electrolyte is protected from direct contact with the water. Contaminants can no longer build up on the surfaces of the electrodes. As a result of its moisture-repellent properties, the membrane cannot be permeated by water. Ionic substances in the water are held back by the membrane, whereas the substance to be determined can pass through the membrane without restriction. The diffusion of the substance through the membrane ensures that the concentrations on both sides of the membrane are equal.

Cell selection is dependent on pressure
Membrane-covered cells can only be used up to a pressure of about 1 bar; and there must be no pressure fluctuations.

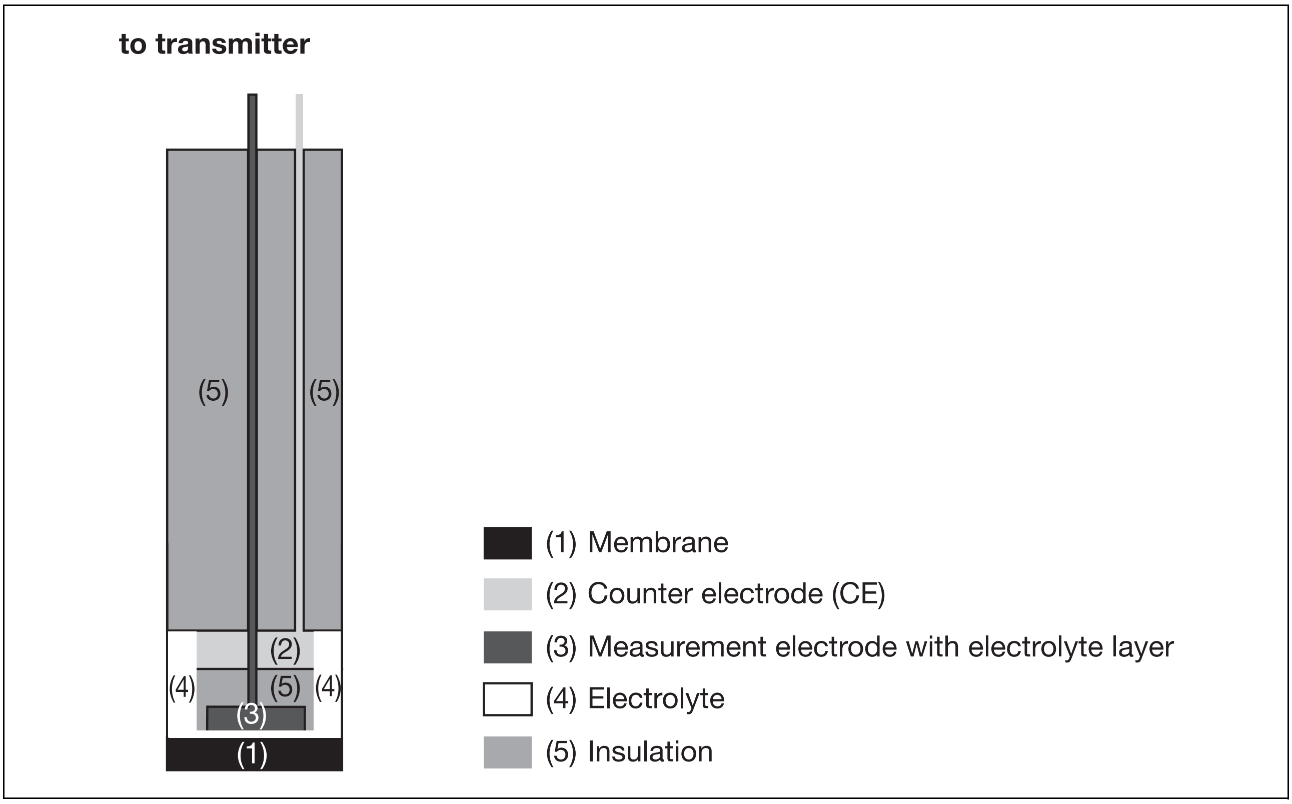

Fig. 4: Schematic representation of a membrane-covered amperometric sensor using the 2-electrode method of construction

Advantages of membrane-covered cells

- no contamination of the electrodes
- defined electrolyte composition in the test chamber
- the measuring signal has low dependence on the flow
- low dependence on the composition of the water to be measured

Note

Because of the defined composition of the electrolyte with a membrane-covered measuring cell, the cell current is equal to zero in the absence of any substance to be analyzed. This avoids the need for a time-consuming calibration procedure. Only the slope has to be determined.

3.5.1 Reactions on metal surfaces, Nernst diffusion layer

To understand the way in which amperometric measuring cells work, it is first necessary to study the transport phenomena that manage the transport of the reacting particles at the electrode surface. To do this, we will examine the flow profile at the surface of an electrode (see Fig. 5):

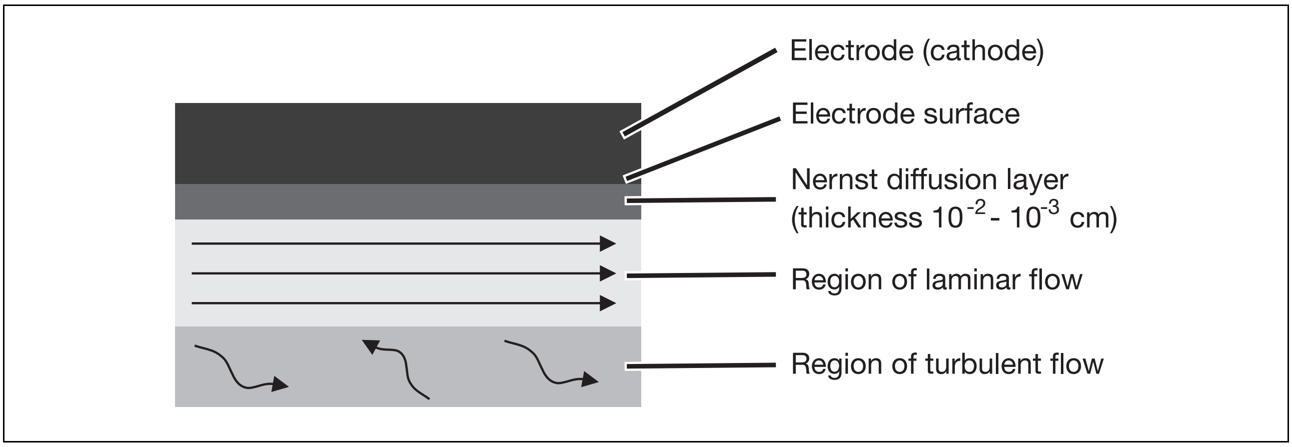

Fig. 5: Flow profile at an electrode surface

In the regions with laminar and turbulent flow, the particle transport occurs through convection. The convection is brought about by agitating or shaking, for example. In the region of the Nernst diffusion layer, the particle transport occurs exclusively through diffusion. Agitation has no effect on the proceedings in the area of the Nernst diffusion layer. Here, the particle transport is accelerated by rising temperature and by lowering viscosity of the medium to be measured.

The thickness of the Nernst diffusion layer (approx. 10^{-2} to 10^{-3}cm) depends on the rate of agitation and the viscosity of the solution.

3.5.2 Two-electrode system

Principle

A 2-electrode system consists of a measuring electrode (ME) and a counter electrode (CE). A certain voltage (polarization voltage) is applied between ME and CE. In an ideal case, only the analyte (that is the disinfectant to be determined) reacts at this voltage. Fig. 6 below shows four different zones:

I no reaction of the analyte at the working electrode, as the applied voltage is too low.

II the reduction of the analyte at the cathode begins, however the applied voltage is still not high enough to reach the zone of the diffusion-controlled limiting current, i.e. not all analyte molecules are reduced immediately at the electrode surface.
The potential associated with point Y (see Fig. 6 and Fig. 7) is called the half-wave potential of the analyte. This potential has a characteristic value for the analyte.

III measuring zone: all the analyte at the electrode surface is reduced immediately. The reaction rate is determined solely by the diffusion of the analyte molecules through the Nernst diffusion layer at the cathode surface.

IV undesirable reactions of oxidizing agents occur, that are more difficult to reduce than the analyte.

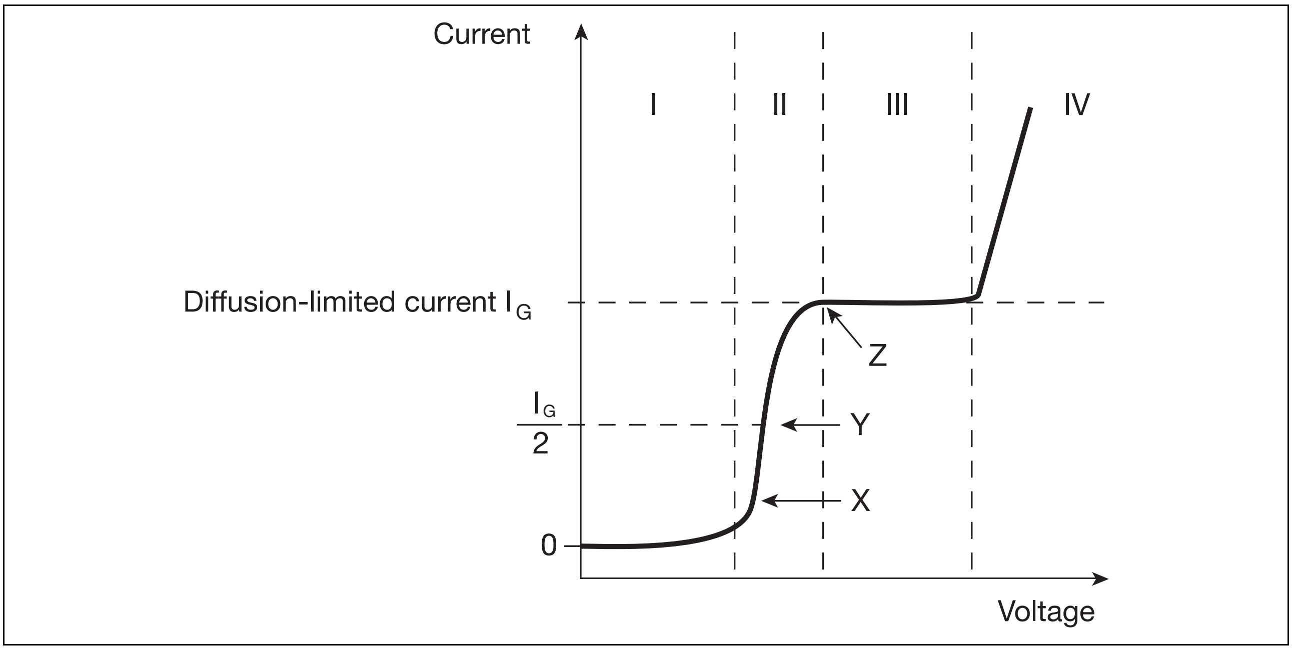

Fig. 6: Schematic representation of current flow with relation to the applied voltage in an amperometric measuring cell

Concentration profile
If we consider the concentration profile of an analyte A at the electrode/solution boundary layer with relation to the distance from the electrode surface, then, in an agitated solution, the following diagram results (see Fig. 7):

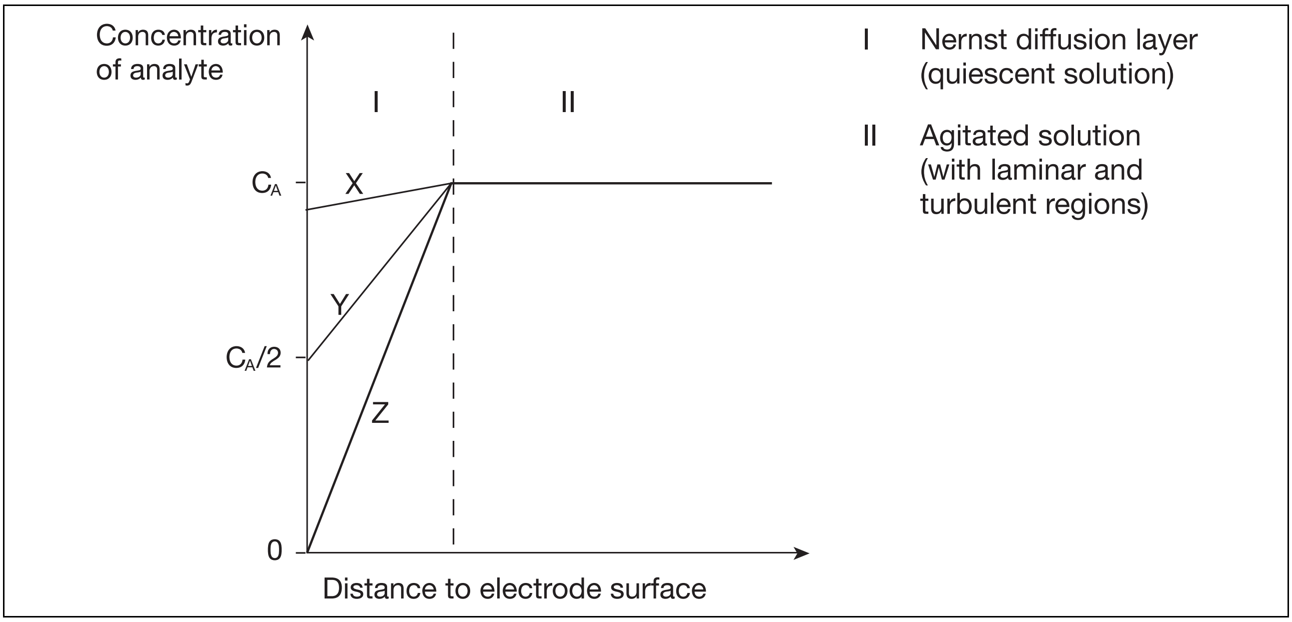

Fig. 7: Concentration profile of analyte A ath the electrode/solution boundary layer (agitated solution)

The X, Y and Z branches of the graph in Fig. 7 correspond to points X, Y and Z in Fig. 6.

After a voltage is applied
analyte A is consumed at the electrode surface and reacts in accordance with the following reaction to form product P:

$$A + n\,e^- \longrightarrow p^{n-}$$

The magnitude of the applied voltage
influences the number of analyte molecules that react at the electrode surface. With voltages in zone III (Fig. 6, voltage ≥ Z), each A molecule reacts immediately it has reached the cathode surface. Hence, the concentration of A directly at the cathode surface is equal to zero. A concentration gradient is created in a thin boundary layer (Nernst diffusion layer) between the measuring or working electrode (ME) and the electrolyte. The species involved have to pass through this boundary layer. The transport process of the analyte through the Nernst diffusion layer at the cathode surface is the slowest and is therefore the rate-determining stage of the overall reaction. Consequently, the speed of the cathode reaction is determined by the subsequent delivery of the oxidizing agent to the cathode surface (concentration polarization). As a result of this, the current flow between anode and cathode is limited (diffusion-controlled limiting current).

Measuring principle
The current (diffusion-controlled limiting current) that flows in zone III (Fig. 6) is proportional to the concentration of the analyte in the medium to be measured. The measured variable is the voltage drop that the current generates across a resistance. The magnitude of the output signal can be varied by the size of the resistance. The output signal is measured by a high-impedance voltmeter or pH meter. After the polarization voltage (zone III, Fig. 6) is applied, a waiting time must be allowed until the equilibrium is reached between electrode and surrounding solution with regard to the subsequent delivery of the analyte to the cathode. This is known as the polarization time, and can be several minutes or even hours, if the sensor is being introduced into the medium for the first time.

3.5.3 Three-electrode system

Stable potential
With the 3-electrode system, the selectivity is increased by the improved stability of the potential: the system consists of the measuring or working electrode (ME), the counter electrode (CE) and a reference electrode (RE). The potential between ME and RE is maintained at the value required for the flow-through reaction by means of a potentiostatic switching arrangement. The RE does not carry any current. The current flows via the CE. Again, in the case of the 3-electrode system, the diffusion-controlled limiting current is proportional to the concentration of the analyte.

A 2-electrode system can also be used for measurement of the analyte, provided that one medium to be measured and of known composition is involved, i.e. only one specific analyte is added.

3.6 Chemical processes at the measuring electrode

The measuring electrode (also referred to as working electrode) is made of a precious metal such as platinum or gold, and is connected as the cathode, i.e. the analyte, as an oxidizing agent, is reduced here. Schematically, taking chlorine as an example:

$$Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-$$

The counter electrode is frequently made of silver. An oxidation takes place as a side reaction at the CE, the anode, e.g.:

$$Ag^0 \longrightarrow Ag^+ + e^-$$

Measurement errors
A 2-electrode system has the disadvantage that the potential between ME and CE can vary. This applies particularly in an open system, as the conditions at the electrodes can vary here, as a result of fluctuations in the composition of the water. If the potential does vary, then other oxidizing agents contained in the water, and having a polarization voltage in a similar range, can also react and distort the result.

3.6.1 Temperature dependence

The diffusion process is temperature-dependent. The diffusion-controlled limiting current increases with rising temperature. With 2-electrode and 3-electrode measuring cells, the temperature dependence can be taken into account by incorporating a temperature sensor. With JUMO sensors, temperature effects specific to the cell are taken into account by suitable NTC resistors.

3.6.2 Calibration procedure

Zero
Normally, the calibration procedure includes the adjustment of zero and slope. However, in the case of membrane-covered sensors, the electrode chamber contains a defined electrolyte, with which the sensor does not exhibit a zero signal. Hence, no zero adjustment using analyte-free water is required in this case. This makes the calibration much simpler, as there is no need to remove the analyte from the measuring medium via an active-carbon filter connected in parallel or similar arrangement.

Slope
To adjust the slope, use is made of an analyte concentration determined by a reference method (e.g. DPD method). The slope is adjusted such that the analyte concentration determined by the reference method is assigned to the voltage signal of the amperometric determination. The sample for determining the reference value should be taken from as close to the sensor incorporation point as possible.

Test systems
Suitable test sets for the determination of free chlorine, chlorine dioxide or ozone are commercially available. Firms supplying test sets that operate on a photometric basis include VWR International (formerly Merck) and Marcherey-Nagel. If necessary, colorimetric test systems can be used, provided that they have the required measuring accuracy. The sample that is used to determine the reference value should be extracted as close as possible to the point where the sensor is fitted.

4.1 Construction of the JUMO measuring cell for free chlorine, chlorine dioxide and ozone

JUMO measuring cells

The JUMO measuring cells are *membrane-covered, amperometric 2-electrode measuring systems* (see Fig. 8). The integral electronics in the shaft supplies an *uncalibrated 4 — 20 mA signal* that can, for example, be further processed by the JUMO dTRANS Az 01 indicator/controller (Data Sheet 20.2550). The instrument takes on two functions: it provides the required supply voltage and permits simple calibration of the measuring system. The cells can also be connected to other indicator, controller, recorder or PLC systems, provided that the supply voltage and calibration allow this. Various measuring ranges are currently available for free chlorine, chlorine dioxide and ozone, see JUMO Data Sheet 20.2630.

Fig. 8: JUMO chlorine measuring cell with the JUMO dTRANS Az 01 indicator and controller

4.1.1 Electrodes

Construction of the 2-electrode measuring cell

The *working electrode* (cathode) is made of gold (Au). The anode, which performs the function of *a combined reference and counter electrode,* is made of silver (Ag), and is provided with a coating of silver chloride (AgCl).

Construction of the 3-electrode measuring cell

3-electrode cells operate on the potentiostatic principle. Reference and counter electrodes are separated. The potential of the reference electrode is particularly constant, as a result of its high impedance. The current flows via the counter electrode. Here too, the working electrode is made of gold and the reference electrode of Ag/AgCl. The counter electrode is made of stainless steel.

4.1.2 Membrane types

The selectivity of the cells can be controlled by the selection of the membrane type:

Hydrophobic, microporous membrane
As a result of their hydrophobic (moisture-repellent) properties, the membranes cannot be wetted by water (or by polar substances generally). In the same way, ionic substances are held back by the membrane. With chlorine measuring cells, this results in, for example, the hypochlorite anions being unable to penetrate the membrane to reach the electrolyte chamber. So the cell does not measure OCl^-. The barrier effect of the membrane applies to substances in both the water to be measured and in the electrolyte chamber.
If the membrane comes into contact with tensides from washing, cleaning or disinfecting agents, the hydrophobic properties of the membrane are lost and the membrane becomes permeable. For that reason, contact with these substances must be strictly avoided. In the same way, contamination of the membrane by dirt or chemicals must be avoided. Cells with hydrophobic, microporous membranes can only be used for water of drinking or swimming pool quality.
Hydrophobic membranes are used in cells for free chlorine, chlorine dioxide and ozone.

In the case of chlorine dioxide and ozone, a membrane that is insensitive to chemicals and tensides can also be used. This option is not available for chlorine, since this membrane type is impermeable to chlorine.

Chemical- and tenside-resistant membrane
This type of membrane does not have any pores. The analyte (ClO_2, O_3) passes through the membrane by means of a “physical dissolution process”. The advantage of this membrane type is its insensitivity to many chemicals, and to tensides.

Any dirt that may have accumulated on the membrane can be gently removed with a brush.

Hydrophilic, microporous membrane
Both polar and ionic substances can pass through this type of (moisture-attracting) membrane. This has the advantage that, here too, the hypochlorite ion can pass through the membrane together with a counter-ion.
Ions from both the water to be measured and from the electrolyte can pass through the membrane. The flow of ions from the water into the electrolyte is desirable. The escape of ions from the electrolyte into the water is undesirable, because, as a result, the electrolyte gradually becomes unable to perform its function. There are various possibilities of slowing down the interchange, and with that the dilution process of the electrolyte:

- increasing the viscosity of the electrolyte
- reducing the aperture area

Of course, these measures will also slow down the speed of response of the measuring cell. In the end, a compromise must be found between service life and speed of response.
Here again, cells with hydrophilic membranes can only be used in water of drinking or swimming pool quality.

A measured medium containing tensides may lead to an accelerated exchange between the electrolyte and the medium. Whether to operate a cell with a hydrophilic membrane in water containing tensides, must be checked in each case, since it is impossible to make general statements about the service life in view of the diversity of the tensides and tenside concentrations used.

The hydrophilic membrane is used in the cell for free chlorine (reduced pH dependency).

4.1.3 Electrolyte

The electrolyte chamber of the electrode (and also its membrane cap) are filled with electrolyte. The reference electrode (with 3-electrode systems) and the combined reference and counter electrode (with 2-electrode systems) develop a constant potential in the electrolyte.
An aqueous solution containing an alkali halide is normally used as the electrolyte. The electrolyte solution can also contain additional components that are crucial for the measuring function. These are, for example, buffer substances in the case of the measuring cell for free chlorine (reduced pH dependency).

4.1.4 Incident flow

A *minimum incident flow velocity* of 15 cm/sec is required to obtain a signal. That corresponds to a flow rate of 30 l/hr if the cell is mounted in a JUMO fitting. Above this minimum incident flow velocity, the measuring signal is only slightly influenced by the flow.

4.1.5 Temperature compensation

The measuring signal of amperometric cells is temperature-dependent. At higher temperatures the membrane becomes more permeable to the analytes and the diffusion-controlled limiting current increases. An automatic *temperature compensation* with an integral NTC resistor compensates for this effect specific to the measuring cell.

4.2 Special cell and membrane types for special applications

4.2.1 Measuring cell for free chlorine with reduced pH sensitivity

Free chlorine occurs in analytes as HOCl and OCl⁻. The ratio of these two different types of chlorine varies with the pH value of the analyte. This behavior is described by the dissociation curve.
Conventional measuring cells (with a moisture-repellent microporous membrane) only respond to HOCl. The OCl⁻ component of the solution to be measured is not taken into account. If the pH value of the solution to be measured changes after the calibration of the cell, a measurement error occurs as a result. When determining free chlorine with conventional cells, the pH value must be kept constant ($\Delta pH \leq 0.05$) after the calibration of the cell. The relationships are explained schematically in Fig. 9 with the help of a graphic.

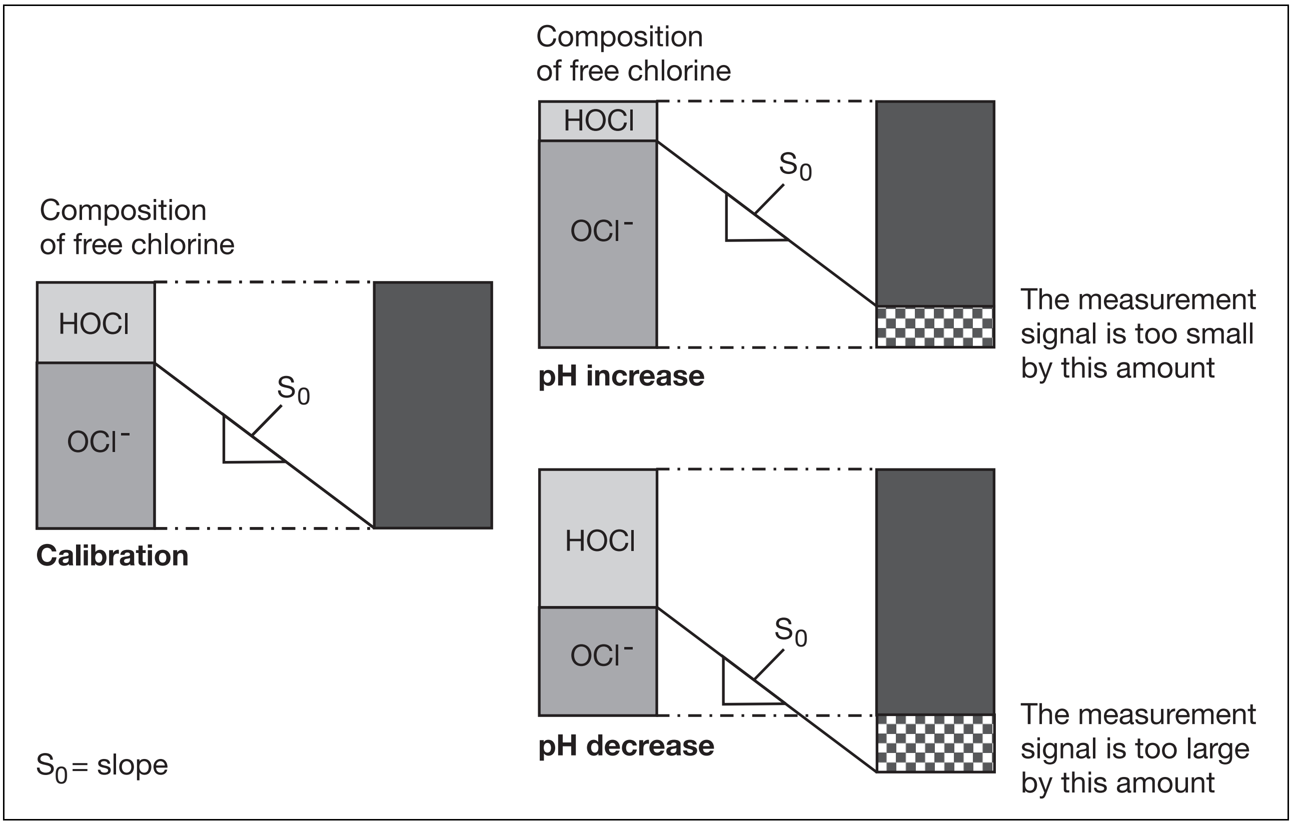

Fig. 9: Schematic effect of pH value changes on the output signal of a conventional measuring cell

- If the pH value of the solution to be measured decreases, then the HOCl component increases and the OCl⁻ component decreases → the measuring signal increases by the amount of the measurement error.
- If the pH value of the solution to be measured increases, then the HOCl component decreases and the OCl⁻ component increases → the measuring signal decreases by the amount of the measurement error.

Measuring cell with reduced pH dependency
If a pH control system is too expensive or not feasible, there is the option of using the JUMO measuring cell for free chlorine (reduced pH dependency).
The hydrophilic membrane of this amperometric cell allows both hypochlorous acid and hypochlorite from the water to be measured to reach the electrode chamber through the membrane. A buffered electrolyte sets a specific ratio of HOCl and OCl⁻ here. As the actual measuring process takes

place in the electrolyte chamber of the cell, the measuring signal is undistorted in the range from pH 5 to 7. In the range from pH 7 to 10.5, the loss in sensitivity (measurement error) is simply 10% per pH increment.

For comparison
At pH 10, the JUMO measuring cell for free chlorine (reduced pH dependency) still supplies about 70% of the original signal for pH 7.
The cell can be used in the range from pH 4 to 12.

At pH 9, a conventional measuring cell for free chlorine only supplies about 5% of the original signal for pH 7. A measurement above pH 8 is practically impossible.

Another advantage of the JUMO measuring cell for free chlorine (reduced pH dependency) is its insensitivity to (iso)cyanuric acid - it also measures the free chlorine formed by the (iso)cyanuric acid. Conventional cells indicate a measured value that is much too small in this case.

Construction of the measuring cell
The JUMO measuring cell for free chlorine (reduced pH dependency) is a potentiostatic 3-electrode sensor with a microporous, hydrophilic membrane and special electrolyte. The working electrode is made of gold, the high-impedance reference electrode of silver/silver halide and the current-carrying counter electrode of stainless steel.

Operating conditions
The cell can be used in water of drinking or swimming pool water quality. The compatibility with tensides must be checked in each case (see chapter 4.1.2 *„Membrane types“*).

Suitable chlorinating agents are, for example, inorganic chlorine compounds such as chlorine gas (Cl_2), NaOCl, $Ca(OCl)_2$, CaCl(OCl) and so on, but also organic chlorine compounds based on (iso)cyanuric acid.
The measured variable is the free chlorine (including "(iso)cyanuric acid chlorine") independent of the (iso)cyanuric acid concentration. Combined chlorine (chloramine) is not measured.

The required incident flow at the membrane is 15 cm/sec, as is also the case with other measuring cells. That corresponds to a flow rate of 30 l/hr if the cell is mounted in a JUMO flow-through fitting.

Zero adjustment/temperature compensation
No zero adjustment is required, as the cell operates without a zero current.
Temperature compensation is integrated in the cell.

4.2.2 Tenside- and chemical-resistant membranes for measurement of chlorine dioxide and ozone

Measuring cells with a hydrophobic, microporous membrane are damaged by tensides (see chapter 4.1.2 *„Membrane types“*). This type of membrane loses its hydrophobic properties due to the effect of the tenside. The water to be measured can enter the electrolyte and electrolyte can escape through the membrane. The function of the cell is impaired.

If the water is polluted with tensides or other chemicals, there is the option of using the JUMO measuring cell with a tenside- and chemical-resistant membrane. Cells with this membrane for measuring chlorine dioxide and ozone can be supplied on request.

The membrane of this particular cell has no pores. The analyte diffuses through the membrane by means of a "physical separation process".
The function is the same as that of a conventional 2-electrode cell.

The operating temperature range is extended to 0 to 55°C as a result of the special membrane.

4.3 Choosing the measuring point, installation and electrical connection of the sensor

The fitting
A special flow-through fitting, optimized with reference to the incident flow at the sensor, is recommended for installation of the JUMO sensors (see Fig. 10).

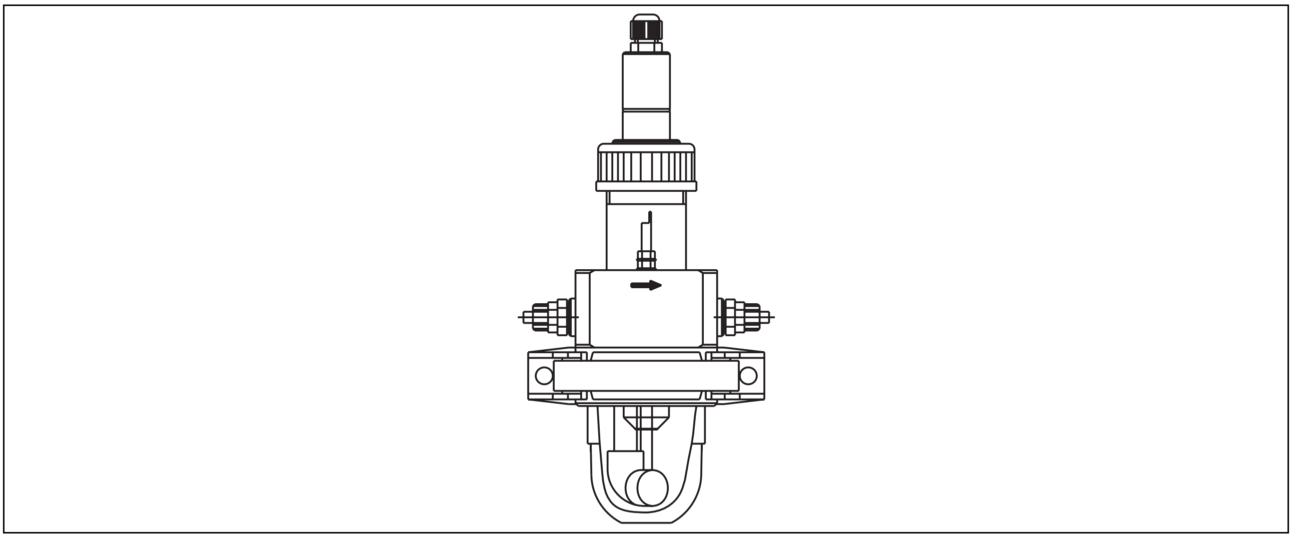

Fig. 10: Flow-through fitting for JUMO sensors

Incident flow
A minimum incident flow velocity of 15 cm/s should be adhered to for the sensor to function correctly; this corresponds to a minimum flow rate of 30 l/hr in the JUMO flow-through fitting. Our flow monitor (1) can be used to check the minimum incident flow velocity. A suitable fitting (2) can be supplied for the flow monitor (see Fig. 11).

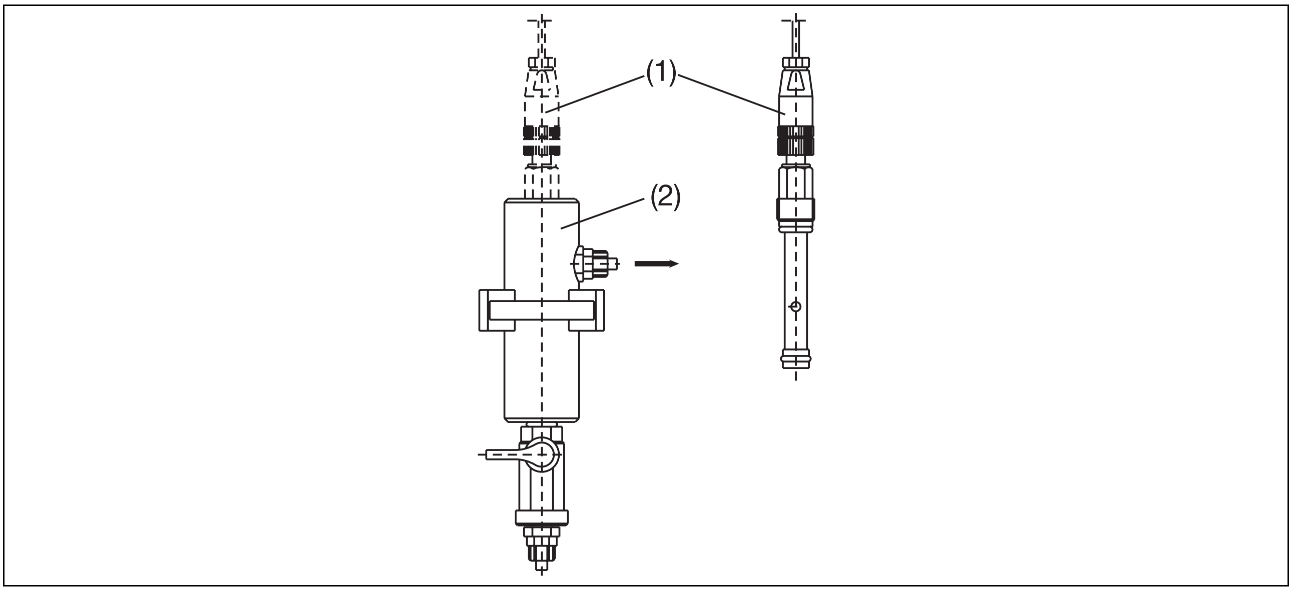

Fig. 11: Checking the flow with a flow monitor

Protective circuit

If the incident flow velocity falls below the minimum permissible value, the optional flow monitor switches the JUMO dTRANS Az 01 indicator/controller into the “Hold” mode, thus avoiding any risk of disinfectant overdose.

The cells can be operated under pressure (up to about 1 bar). This makes it simple to recirculate the water.

The 4 — 20 mA 2-wire connection is used for the supply to the cell (24 V DC), and also for the transmission of the uncalibrated measuring signal to the evaluation instrument. The cells can be connected to any indicator, controller, recorder or PLC system, provided that these can take on the functions described above.

4.4 Applications of the amperometric measurement of chlorine, chlorine dioxide and ozone

Requirements
The use of a membrane-covered amperometric sensor requires a certain water quality. The water concerned must be **drinking water, swimming pool water or water of similar quality to drinking water. With heavily polluted water, the correct functioning of the sensor can be impaired by fouling of the membrane.** A membrane-covered sensor can be used in the following areas:

- drinking water
- swimming pool water
- process and production water, water used for industrial purposes
- circulating systems such as coolant circuits, for example

Exception
An exception are cells with a membrane that is insensitive to chemicals and tensides, see chapter 4.2.2 *„Tenside- and chemical-resistant membranes for measurement of chlorine dioxide and ozone“*. These cells can also be used in water polluted by tensides and chemicals (inferior quality to drinking or swimming pool water) and are available on request for chlorine dioxide and ozone, but not for chlorine.

4.5 Incompatibility with the measured medium

Conventional membrane-covered cells[1] are **incompatible** with

- **tensides** (surfactants, detergents etc.): if the moisture-repellent membrane of a measuring cell comes into contact with tensides, this leads to the condition where the membrane can subsequently be wetted by water. As a consequence, the water can pass through cavities in the porous polymer membrane, with the result that the electrolyte inside the measuring cell is diluted and the measuring signal starts to drift. Additionally, the loss of the moisture-repellent properties leads to a condition where the membrane can now be permeated by ionic components on both sides of the membrane.
  In the case of the cell for free chlorine with a reduced pH dependency (Type 202630/41, with hydrophilic membrane) it must be checked individually whether the service life of the cell is in any way restricted by the tenside.
- **moisture-repellent substances** (e.g. mineral oils etc.): moisture-repellent substances can penetrate into the porous membrane, clogging up the porous structure, and so making the transfer of analyte difficult or even impossible.

In beiden Fällen wird der Sensor in seiner Funktion gestört.
Reinigung der Messzelle oder Austausch von Membrane und Messzellenelektrolyt können diese Störungen beheben. Vor einem erneuten Einsatz der Messzelle müssen die störenden Substanzen aus dem Messwasser entfernt oder das Wasser komplett ausgetauscht werden.

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[1] Anexception are cells with a membrane that is insensitive to chemicals and tensides, see chapter 4.2.2 *„Tenside- and chemical-resistant membranes for measurement of chlorine dioxide and ozone“*.

4.6 Errors and faults during measurement with amperometric sensors

Error	Cause	Remedy	Preventive measures
(1) Sensor value too low.	Incorrect calibration.	Repeat calibration with DPD method.	If necessary, calibrate sensor more often.
	pH value during measurement is higher than during calibration (only with chlorine).	Maintain constant pH value during measurement and calibration, ∆pH ≤ 0.05.	Improve pH control. If necessary, use sensor with reduced pH dependency.
(2) Sensor value too low; sensor cannot be adjusted to DPD value.	Coating on the tip of the electrode finger.	Abrade the tip of the electrode finger with the special sandpaper supplied, fill up with new electrolyte (always follow operating instructions!).	Shorten maintenance intervals.
	Incident flow at sensor is too low	Provide increased and improved incident flow at the sensor.	
(3) As (2), or also when the sensor value falls or remains constant as the DPD value increases.	Destruction of the membrane: electrolyte escapes / water enters.	Abrade the tip of the electrode finger with the special sandpaper supplied. Fill up with new electrolyte. Renew membrane cap. (always follow operating instructions!). If the measuring cell still does not function, it could be that the surface coating on the anode / reference electrode is damged. In this case, the measuring cell must be returned to the manufacturer.	Avoid damage to membrane. Avoid knocking sensor when membrane cap is unscrewed. Avoid inflow of coarse particles or fragments of glass.
	Effect of tensides from detergents and cleansing agents on the membrane. The membrane loses its moisture-repellent properties; water or ions can pass through it. Exception: Measuring cells with membranes that are immune to chemicals and tensides (not for chlorine).	As (3), but, in addition, a change of water is necessary before the chlorine sensor is used again (to remove all traces of tensides).	Avoid effects of tensides on the membrane, ensure that all traces of cleansing agent and other disinfectant are fully washed away after cleaning the plant.
(4) Sensor value too high compared with DPD.	Incorrect calibration.	Repeat calibration with DPD method.	If necessary, calibrate sensor more often.
	pH value during the measurement is lower than during the calibration (only with chlorine).	Maintain constant pH value during measurement and calibration (∆pH ≤ 0.05).	Improve pH control. If necessary, use sensor with reduced pH dependency.

Error	Cause	Remedy	Preventive measures
(5) Sensor value too high compared with DPD. Sensor cannot be adjusted to DPD value.	Additional oxidizing agents contained, as well as the analyte, e.g. Cl_2, ClO_2, O_3, H_2O_2, chlorine in the form of cyanuric acid, etc.	Refrain from addition of these substances, change water.	Ensure that cleansing agents and disinfectants are fully removed after use. Only use one disinfectant, e.g. NaOCl, $Ca(OCl)_2$, CaCl(OCl), ClO_2, O_3, Cl_2 (also produced electrolytically).
(6) DPD and sensor values agree, trend redox measurement is correct, but setpoint value is not maintained.	Incorrect control parameter	Optimize control parameter	
	Amount of disinfectant being dosed per unit time is too high, concentration overrun before the water to be measured reaches the cell.	Reduce amount added per unit of time, reduce concentration of disinfectant in the solution added.	
	Flow through plant is too slow.	Improve mixing.	Modify structure to improve mixing.
(7) Sensor value and DPD value do not agree. Sensor values fluctuate: too much / too little. Trend of the redox measurement does not agree with the sensor value.	Incorrect control parameter for acid dosing (specific to chlorine).	Optimize control parameter.	
	Amount of acid being dosed per unit time is too high. Overacidity occurs, before the water to be measured has reached the pH electrode (specific to chlorine).	Reduce amount of acid added per unit of time, reduce concentration of acid in the solution added.	
	Flow through plant is too slow.	Improve mixing.	Modify structure to improve mixing.
(8) Unusually sluggish response of the sensor.	Membrane partially blocked by contaminants such as lime or oil. Access of the disinfectant to the sensor is obstructed.	Change membrane and electrolyte, clean electrode finger (always follow operating instructions!)	Take steps to improve the water quality.
(9) Fluctuating measured value	Supply failure		
	Analyte has built up in the electrolyte.	Wait until the analyte has been decomposed at the cathode. If that takes too long: change electrolyte.	
(10) No calibration possible	Wrong electrolyte added.	Change electrolyte. Clean with water and dry beforehand.	Store electrolyte systematically to avoid confusion.
(11) Measured value fluctuations (e.g. when withdrawing a water probe from a pipe carrying the water to be measured)	Pressure fluctuations are moving the membrane up and down.	Provide constant pressure ratio.	Measurement in "open outlet" at atmospheric pressure.

5 References

5.1 Standards and regulations concerning the treatment of water with chlorine, chlorine dioxide and ozone

DIN 19 627	Ozone production plants for the treatment of water
DIN 19 643-1	Treatment of swimming and bathing pool water – Part 1: General Requirements
DIN 19 643-2	Treatment of swimming and bathing pool water – Part 2: Process combination: Adsorption, Flocculation, Filtration, Chlorination
DIN 19 643-3	Treatment of swimming and bathing pool water – Part 3: Process combination: Flocculation, Filtration, Ozonization, Sorption filtration
DIN 19 643-4	Treatment of swimming and bathing pool water – Part 4: Process combination: Flocculation, Ozonization, Multi-layer filtration, Chlorination
DIN 19 643-5	Treatment of swimming and bathing pool water – Part 5: Process combination: Flocculation, Filtration, Adsorption by activated carbon granules, Chlorination
DIN 38 408-3	Determination of ozone
DIN 38 408-5	Determination of chlorine dioxide
DIN EN 937	Products for the treatment of water intended for human consumption – chlorine
DIN EN 1278	Products for the treatment of water intended for human consumption – ozone
DIN EN 12 671	Products for the treatment of water intended for human consumption - chlorine dioxide
DIN EN ISO 7393-1	Water Quality – Determination of free chlorine and total chlorine – Part 1: Titrimetric method with N,N-diethyl-1,4-phenylendiamine
DIN EN ISO 7393-2	Water Quality – Determination of free chlorine and total chlorine – Part 2: Colorimetric method with N,N-diethyl-1,4-phenylenediamine for routine checks
DIN EN ISO 7393-3	Water Quality – Determination of free chlorine and total chlorine – Part 3: Iodometric method for determination of total chlorine
ISO 7393-1	Water Quality – Determination of free chlorine and total chlorine – Part 1: Titrimetric method with N,N-diethyl-1,4-phenylenediamine
ISO 7393-2	Water Quality – Determination of free chlorine and total chlorine – Part 2: Colorimetric method with N,N-diethyl-1,4-phenylenediamine for routine checks
ISO 7393-3	Water Quality – Determination of free chlorine and total chlorine – Part 3: Iodometric titration method for determination of total chlorine
	Drinking Water Regulations - Regulations concerning drinking water and water for food processing plants, in the version as published 5 December 1990
	Regulation concerning the quality of water intended for human consumption, German Safe Drinking Water Act - TrinkwV 2001 (amendment to TrinkwV dated May 21, 2001, national implementation of 98/83/EC).
	Bundesgesundheitsblatt 45 (2002) 10, 827-845, „Liste der Aufbereitungsstoffe und Desinfektionsverfahren“ as per §11 TrinkwV 2001 (List of treatments and methods of disinfection, Federal Health Gazette).
	76/160/EEC Council Directive of 8 December 1975 concerning the quality of bathing water, OJ (Offical Journal) of 5 February 1976, No. L 31 S. 1, finally amended by Directive 91/692/EEC of 23 December 1991, OJ of 31 December 1991, No. L 377 S. 48

79/869/EEC – Council Directive of 9 October 1979 concerning the reference methods of measurement and frequency of sampling and analysis of surface water intended for the abstraction of drinking water in the Member States, OJ of 29 October 1979, No. L 271 S. 44

80/778/EEC - Council Directive of 15 July 1980 concerning the quality of water intended for human consumption, OJ of 30 August 1980, No. L 229 S.11

98/83/EC - Council Directive of 3 November 1998 concerning the quality of water intended for human consumption, OJ EC No. L300 S.32

2000/60/EG – Directive of the European Parliament and Council issued on 23 October 2000 to establish a framework for Community activities in the field of water policy, OJ of 22 December 2000, No. L 327 S.1

5.2 Literature

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- Office of Water, United States Environmental Protection Agency (EPA) Guidance Manual: Alternative Disinfectants and Oxidants, April 1999.

Note
Information about **occupational safety and general information on chlorine, chlorine dioxide, ozone, sodium hypochlorite solution, etc.**, can be found in the GESTIS-Stoffdatenbank des Berufsgenossenschaftlichen Instituts für Arbeitssicherheit (GESTIS substance database, Social Insurance Institute for Occupational Safety and Health). Information can be obtained from the Internet at the following address: http://www.hvbg.de/

5.3 Closing remarks

The facts dealt with in this technical publication represent the current state of knowledge in the fields of measurement, standards and legal requirements.

JUMO is continually developing its products and, in doing so, takes account of the current requirements and latest developments in the world of standards.

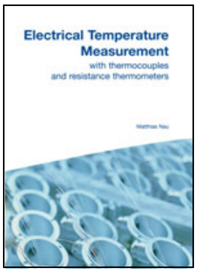
In the field of standards and legal requirements, the details they contain about pemissible disinfectants, disinfectant concentrations and their by-products, may be changed in future by the responsible public authorities. For this reason, if there is any doubt, the **current** legal requirements, directives and standards are definitive.

Informative material from JUMO – for beginners and those with some practical experience

Know-how is not just needed to create JUMO products, but also for their later application.
That is why we offer several publications on aspects of measurement and control engineering for our users.

The publications are intended to provide step-by-step familiarization with a wide range of applications, for both beginners and those with some practical experience. They primarily illustrate general topics with JUMO-specific applications to some extent.

In addition to JUMO technical literature and our new software downloads we also offer the possibility to order our brochures and CD-ROM catalogs online.



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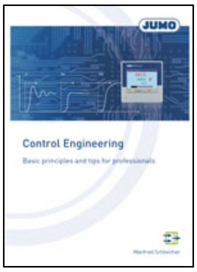

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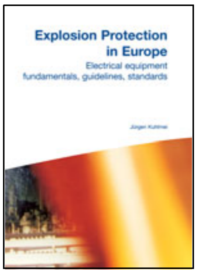

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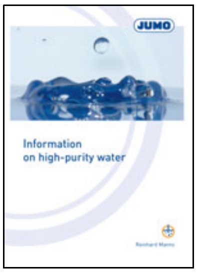

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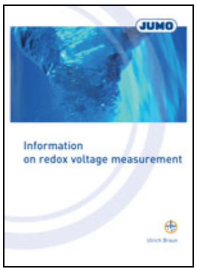

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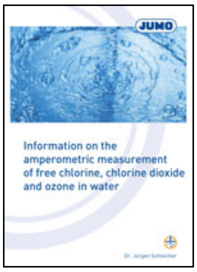

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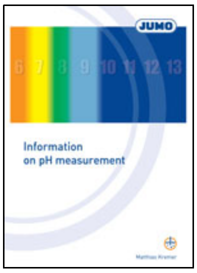

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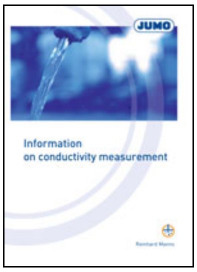

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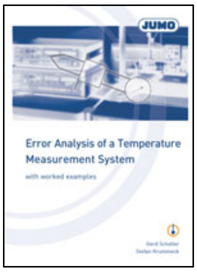

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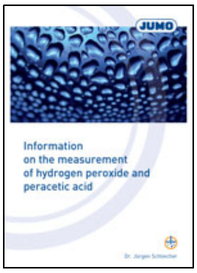

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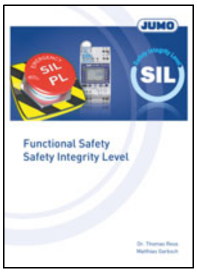

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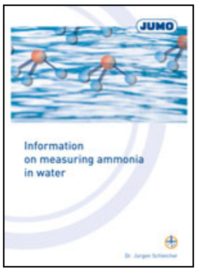

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