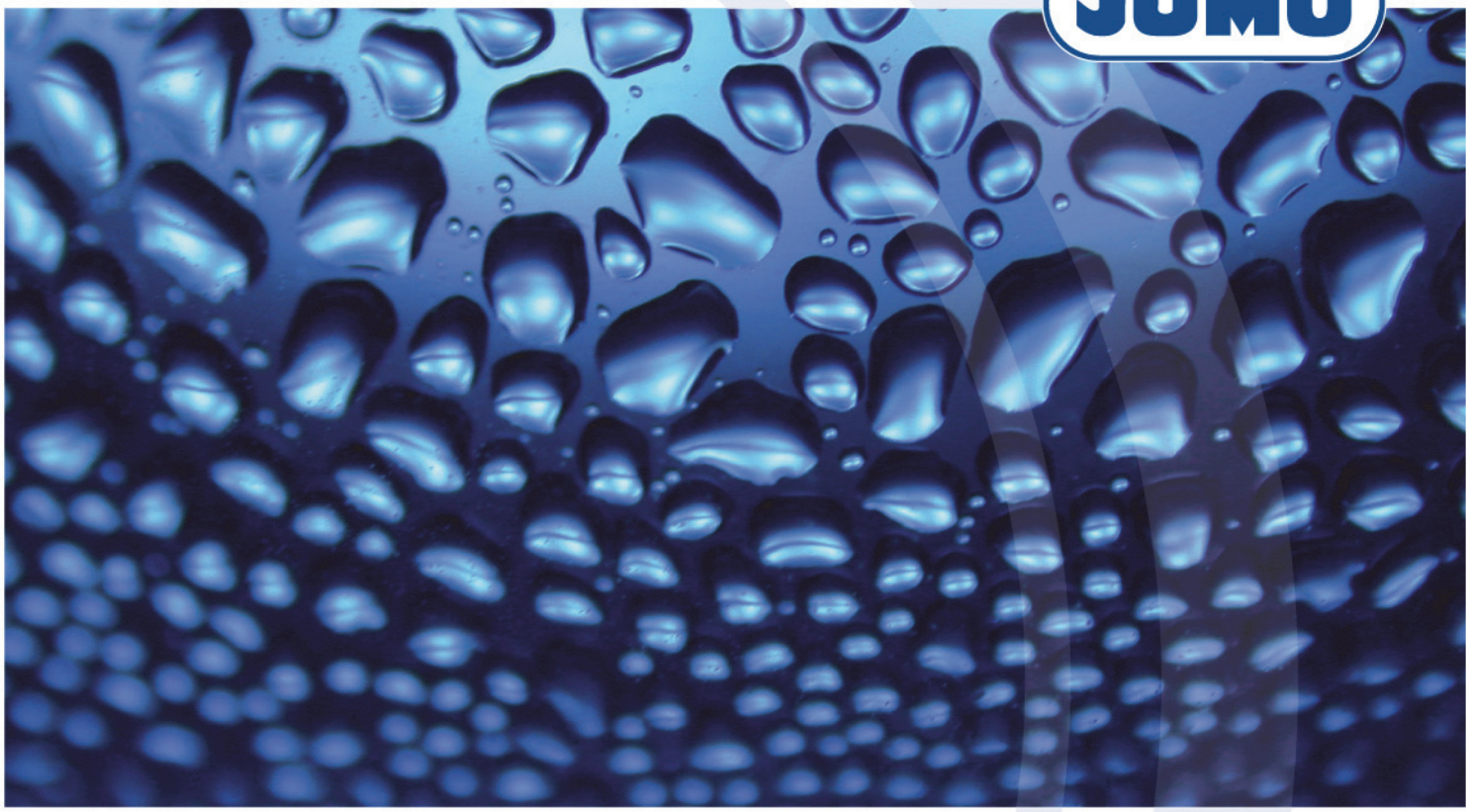

Information on the measurement of hydrogen peroxide and peracetic acid

Dr. Jürgen Schleicher

Information on the Measurement of Hydrogen Peroxid and Peracetic Acid

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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

We try to ensure that the “Information on the Measurement of Hydrogen Peroxide and Paracetic Acid” is always kept fully up to date. In case of any doubt or discrepancy, please refer to the currently valid regulations and relevant standards. We invite our readers to share their experience and knowledge. Any comments or contributions for discussion will be most welcome.

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Contents

1 Introduction

1.1 Hydrogen peroxide

Hydrogen peroxide is applied, for instance, in the sterilization of the surfaces of primary packaging that is used for the aseptic filling of food. The hydrogen peroxide is usually stabilized by suitable additives to prevent decomposition, such as sodium phosphate and stannate, chelate formers, sulfuric acid, phosphoric acid and the like. An undesirable decomposition of the hydrogen peroxide into water and oxygen can be caused by metals, alkalis and dust.

1.2 Peracetic acid (PES)

Peracetic acid (referred to below as PAA) is used, for instance, in the chemical industry, paper and cellulose industry, food and beverage production, and pharmaceutical sector, as a reagent, disinfectant, or sterilizing agent.

It is also possible for PAA to decompose. This is accelerated by elevated temperatures and traces of heavy metals, such as iron or copper.

PAA has the chemical formula $CH_3CO\text{-}OOH$ and is produced by the reaction of acetic acid with hydrogen peroxide.

2 Analytical determination

2.1 for hydrogen peroxide

Hydrogen peroxide cannot be determined by the DPD method (as can chlorine, for instance). Potentially usable methods of determination include various titration procedures using manganese or iodine compounds:

- DIN 38 409-15 „Bestimmung von Wasserstoffperoxid“ (Determination of hydrogen peroxide)
- ISO/DIS 7157 „Determination of the hydrogen peroxide concentration - titrimetric method“

or:

- Ph.Eur. (European Pharmacopeia), monograph
  „Hydrogen peroxide: determination of the concentration“

2.2 for peracetic acid

Basically, the same methods can be applied for PAA as for hydrogen peroxide, provided that the molecular weight of PAA is taken into account.

A method for the determination of PAA can be found on the Internet, for example at the following address: https://www.peroxygen-chemicals.net

2.3 Continuous measurement method for hydrogen peroxide and PAA

Continuous measurement
The methods of determination mentioned above are **not** continuous (online) measurements methods, but methods whereby the concentration is measured for samples taken at certain times.

These analytical methods are laboratory procedures requiring a considerable outlay in personnel and time.

In order to regulate the concentration of a disinfectant, it is advantageous if a electrical signal is available that is continuous and proportional to the concentration of disinfectant. This signal can then be used as the input signal for controlling a disinfectant metering system, i.e. the concentration can be completely automatically regulated.

A membrane-covered amperometric measuring cell can be used for monitoring the **peracetic acid concentration** and the **concentration of hydrogen peroxide**.

3 Measurement of hydrogen peroxide/peracetic acid

One possibility for continuous measurement of the concentration of hydrogen peroxide and peracetic acid is electrochemical determination by amperometric sensors.

Principle of measurement
Hydrogen peroxide/peracetic acid reacts at the working electrode (cathode). The current that is measured is proportional to the concentration of the substance being analyzed in the solution.

Implementation
The basic design of amperometric sensors operating on the 2-electrode principle is shown in Fig. 1.

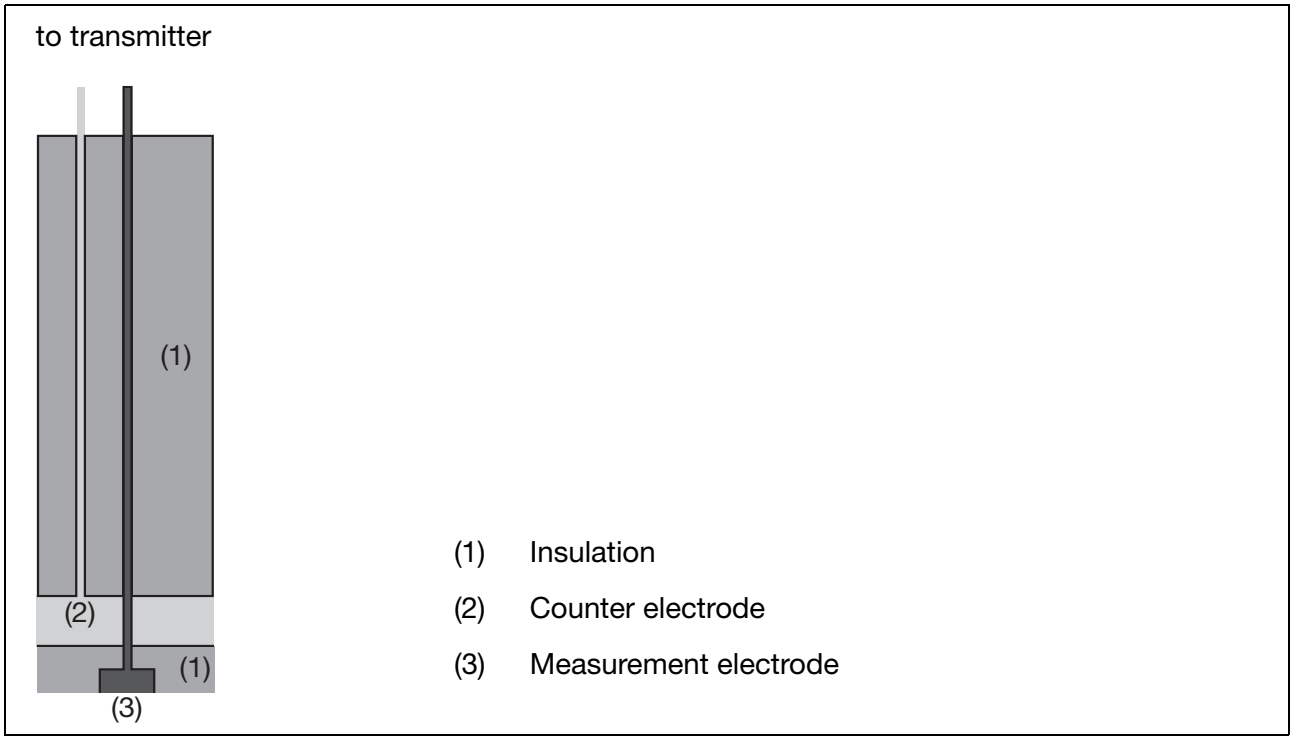

Fig. 1: Schematic representation of an amperometric sensor in 2-electrode design

These sensors are available in both open and membrane-covered versions. As membrane-covered measuring cells offer a number of advantages, JUMO only offers this type of sensor.

Direct electrode contact
with the water being analyzed can lead to inactivation of the electrode as a result of dirt deposits or collateral electrochemical reactions. In this situation, it will be necessary to apply continuous cleaning of the electrodes, by means of quartz, glass or Teflon pearls. The water being analyzed flows into a special flow-through fitting that agitates the cleaning pearls, and the continuous contact of these pearls with the electrode surfaces keeps them free of contamination. JUMO does not offer “open” systems.

3 Measurement of hydrogen peroxide/peracetic acid

Protected
An alternative method of preventing contamination of the electrodes is to cover the measuring cell by a membrane (Fig. 2), thus preventing direct contact between the electrode space, which is filled with an electrolyte, and the water being measured. Contamination can no longer be deposited on the surfaces of the electrodes, but the substance being analyzed can freely penetrate the membrane. Diffusion of the substance being analyzed through the membrane ensures that its concentration is equalized on both sides of the membrane.

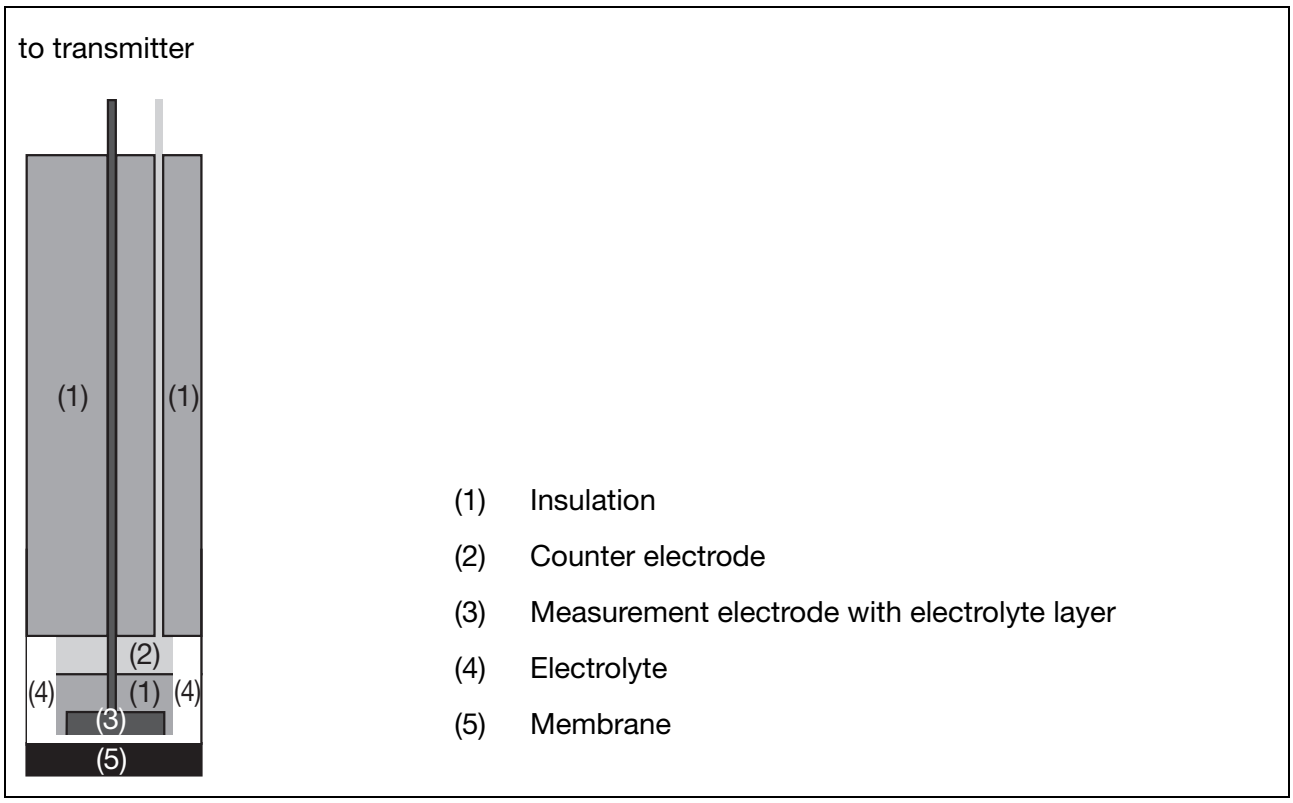

Fig. 2: Schematic representation of a membrane-covered amperometric sensor in 2-electrode design

Advantages of membrane-covered cells

- no contamination of the electrodes
- defined electrolyte composition in the sample space
- measurement signal is only weakly flow-dependent
- low sensitivity to the composition of the water being analyzed

Note
The defined composition of the electrolyte in a membrane-covered measuring cell means that the cell current is zero if the substance being analyzed is not present. This avoids an involved calibration procedure. It is only necessary to determine the slope.

3 Measurement of hydrogen peroxide/peracetic acid

3.1 Reactions on metal surfaces, the Nernst diffusion layer

In order to understand the operation of amperometric measuring cells, it is necessary to take a look at the transport mechanisms that govern the transport of the reactive particles on the surface of the electrode. Let's look at the profile of the flow across the surface of an electrode (Fig. 3):

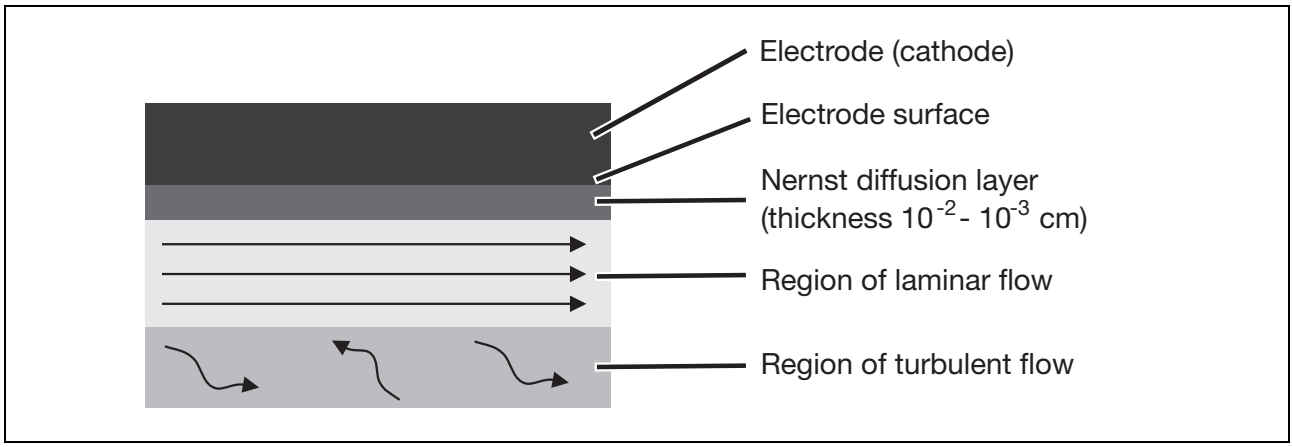

Fig. 3: Flow profile across an electrode surface

The transport of particles in the regions with laminar and turbulent flow takes place by convection. This convection is stimulated by agitation through shaking or stirring. In the region of the Nernst diffusion layer, transport takes place exclusively through diffusion. Agitation has no effect on the processes in the region of the Nernst diffusion layer. The transport of particles in this region is accelerated by a higher temperature or lower viscosity of the medium being measured.

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

3.2 2-electrode system

Principle
A 2-electrode system consists of the measuring electrode (ME) and the counter-electrode (CE). A specific voltage (the polarization voltage) is applied between the ME and CE. In an ideal situation, only the substance being analyzed (i.e. the disinfectant) will respond at this voltage. The following Fig. 4 shows four distinct regions:

I No response of the substance being analyzed at the measuring/working electrode, since the applied voltage is too low.

II The substance being analyzed starts to be reduced at the cathode, but the applied voltage is not high enough to reach the region of diffusion-limited current, i.e. not all the molecules of the substance being analyzed are instantly reduced at the electrode surface.
The voltage corresponding to Y (Fig. 4 and 5) is also known as the “half-wave potential” of the substance being analyzed. This potential has a characteristic value for the particular substance.

III Measuring range: All of the substance being analyzed is instantly reduced at the electrode surface. The speed of the reaction is determined solely by diffusion of the molecules of the substance through the Nernst diffusion layer at the surface of the cathode.

IV Undesirable reactions of oxidizing agents that are more difficult to reduce than the substance being analyzed occur in this region.

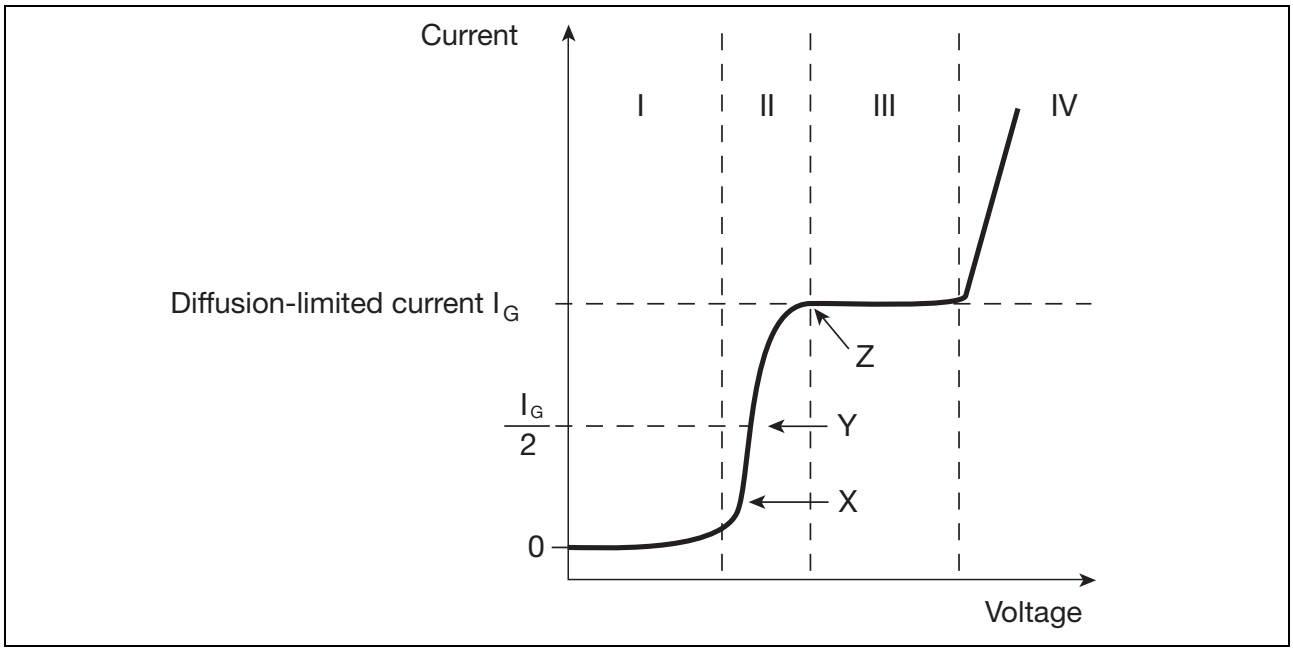

Fig. 4: Schematic representation of the flow as a function of the applied voltage in an amperometric measuring cell

3 Measurement of hydrogen peroxide/peracetic acid

Concentration profile
If you look at the profile of the concentration of a substance A in the boundary layer between the electrode and the solution, as a function of the distance to the electrode surface, then the following picture will be obtained in an agitated solution (Fig. 5):

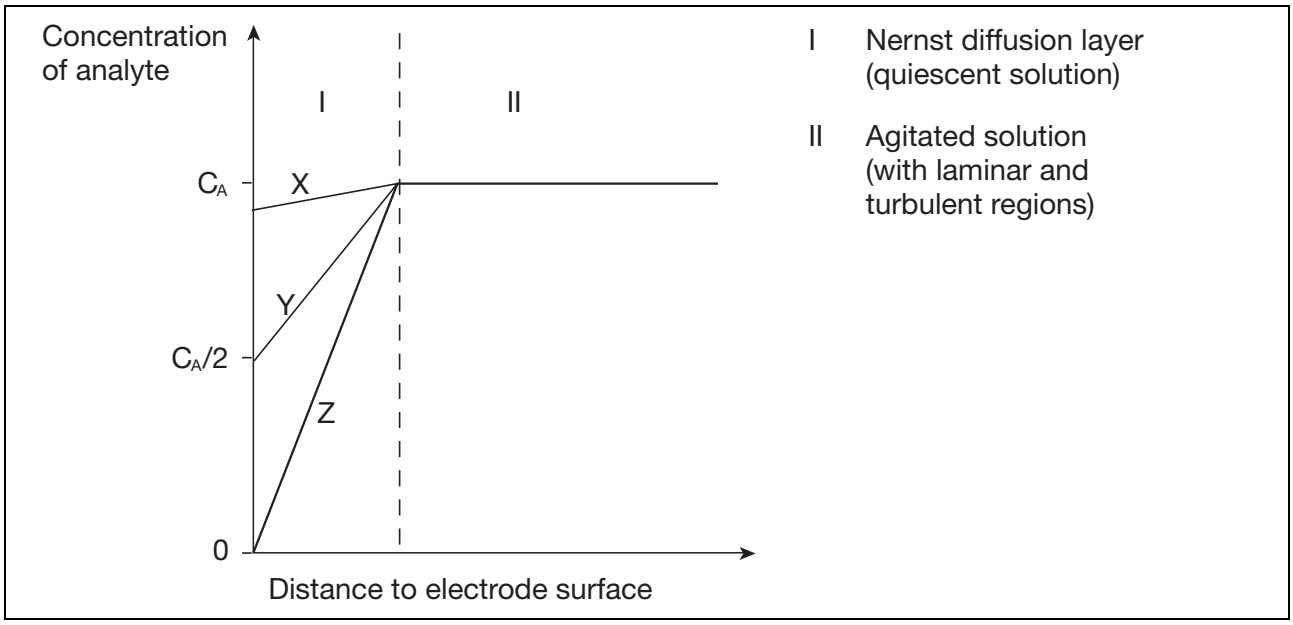

Fig. 5: Concentration profile of substance A at the electrode/solution boundary (agitated solution)

The branches X, Y and Z of the curve in Fig. 5 correspond to the points X, Y and Z in Fig. 4.

When a voltage is applied
then substance A is consumed at the surface of the electrode, and is converted to the product P in accordance with the following reaction equation:

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

The magnitude of the applied voltage
influences the number of molecules of the substance that react at the surface of the electrode. At voltages in region III (Fig. 4, Voltage ≥ Z) revery molecule reacts instantaneously when it reaches the surface of the cathode. So the concentration of substance A is zero on the surface of the cathode. The result is a gradient of concentration of the substance being analyzed (A) throughout a thin boundary layer (the Nernst diffusion layer) between the measuring/working electrode (ME) and the electrolyte. The substance involved must penetrate this boundary layer. The transport process for the substance through the Nernst diffusion layer to the cathode surface is the slowest part of the overall reaction, and therefore the factor that determines the overall speed. The speed of the reaction at the cathode is thus determined by the refreshing of the oxidizing agent at the surface of the cathode (polarization of concentration). This limits the flow of current between the anode and cathode (diffusion-limited current).

Principle of measurement
The current that flows in region III (Fig. 4) (diffusion-limited current) is proportional to the concentration of the substance being analyzed in the measured solution. The measurement variable is the voltage drop produced by the current across a resistance. The magnitude of the output signal can be varied by altering the value of the resistance. The output signal is measured by a high-impedan-

ce voltmeter or pH-meter. After applying the polarization potential (region III, Fig. 4). It is necessary to wait a certain time until equilibrium has been achieved between the electrode and the surrounding solution with regard to the refreshing of the substance being analyzed at the cathode. This time, known as the polarization time, can be several minutes, or even hours, when the sensor is immersed in the medium for the first time.

3.3 Chemical processes at the measuring electrode

The measuring electrode (also known as the working electrode) consists of a noble metal, such as platinum or gold, and is used as the cathode in the circuit, i.e. the substance being analyzed is reduced as an oxidizing agent. The counter-electrode is frequently made of silver. At the CE, oxidation takes place, as a counter-reaction.

3.4 Temperature dependency

The diffusion process is temperature-dependent. The diffusion-limited current increases as the temperature rises. This temperature-dependency can be taken into account by incorporating a temperature sensor. In JUMO sensors, temperature effects that are specific to the measuring cells are compensated by corresponding NTC resistors.

3.5 Calibration procedure

Zero point
The calibration procedure normally covers the adjustment of the zero point and the slope. However, when using membrane-covered sensors, the electrode space is filled by a defined electrolyte and the sensor does not have a zero signal. So a zero point adjustment using water that is free from any analytical substances is not required. This makes calibration considerably simpler, since it is **not** necessary to remove the analytical substance from the medium before calibration.

Steilheit
The slope is adjusted by using a known concentration of the substance that has been measured by a reference method (Chapter 3.1 *„Reactions on metal surfaces, the Nernst diffusion layer“*). The slope is adjusted so that the uncalibrated signal current in the amperometric measuring cell is matched to the known concentration of the substance that was established by the reference method.

4 Instrumentation

4.1 Design of the JUMO cell for hydrogen peroxide/peracetic acid

JUMO measuring cells
The JUMO cells are **membrane-covered, amperometric 2-electrode systems** (Fig. 6). The electronics integrated in the shaft of the cell provides an **uncalibrated 4 — 20 mA signal**, that can, for example, be processed by the JUMO dTRANS Az 01 indicator/controller (Data Sheet 20.2550). The instrument has two functions: It supplies the necessary voltage and permits simple calibration of the measurement system. However, the cells can also be connected to different indicating/control/recording or PLC systems, as long as they provide the correct supply and allow calibration. The cells are available for various measurement ranges



Fig. 6: JUMO dTRANS Az 01

4.1.1 Electrodes

Design of the 2-electrode cell
The **working electrode** (cathode) consists of gold (Au). The anode, which functions as a **combined reference and counter-electrode**, is made of silver (Ag) and has a silver halide coating.

4.1.2 Elastic membrane

The elastic membrane is not porous. The substance being analyzed must penetrate the membrane in the form of a solution. One advantage of this membrane is its insensitivity to chemicals and tensides. This type of membrane is used in the measuring cells for hydrogen peroxide and peracetic acid, but is also suitable for cells for measuring chlorine dioxide and ozone. Special measuring cells are available on request.

4.1.3 Electrolyte

The electrolyte space in the electrode and its membrane cap is filled with electrolyte. The combined reference and counter-electrode establishes a constant potential in the electrolyte.
An alkaline-halide solution is used for the electrolyte. The electrolyte solution may also contain other constituents that are important for the measuring function.

4.1.4 Incident flow

A **minimum flow velocity** of 15 cm/sec onto the surface of the sensor (i.e. incident flow) is required to obtain a signal. This corresponds to a volume flow of 30 liters/hour, when the measuring cell is built into a JUMO fitting. The measuring signal is only slightly flow-sensitive above this minimum incident flow velocity.

4.1.5 Temperature compensation

The measuring signal from amperometric cells is temperature-dependent. If the temperature rises, the membrane is more permeable for the substance being analyzed and the diffusion-limited current increases. This cell-specific effect is countered by an automatic **temperature compensation** provided by an integrated NTC resistor.

4.2 Choose the measurement point, installation and electrical connection

Fitting

A special flow-through fitting (Fig. 7) is recommended for mounting JUMO sensors, which has been optimized for the incident flow onto the sensor.

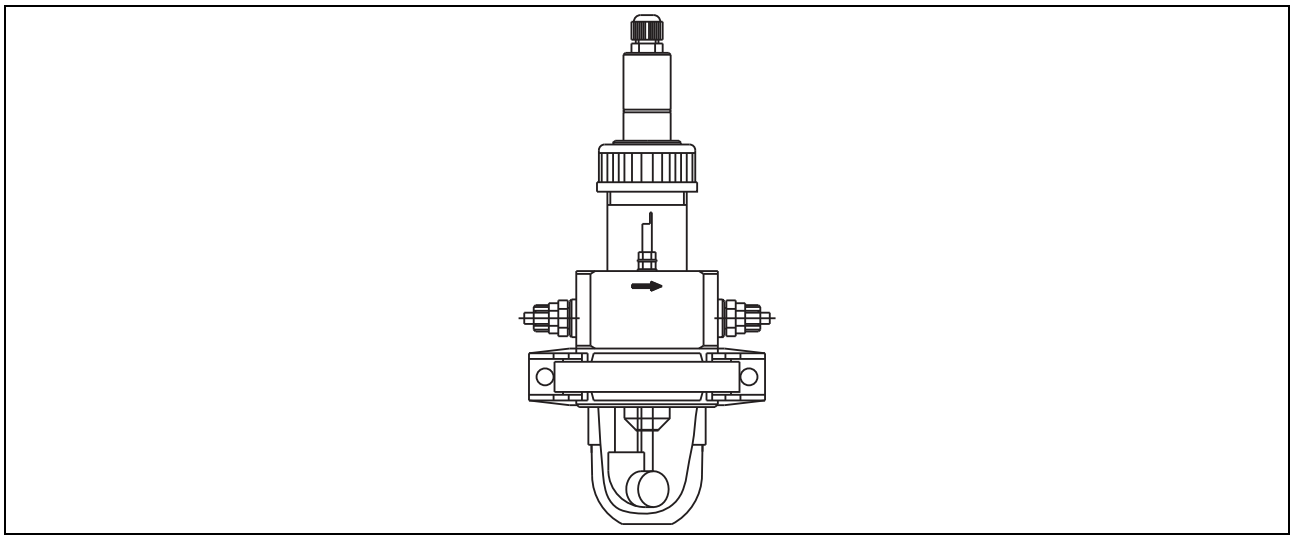

Fig. 7: Flow-through fitting for JUMO sensors

Incident flow

For correct functioning of the sensors, a minimum incident flow velocity of 15 cm/sec must be maintained, corresponding to a minimum flow volume of 30 liters/hour in the JUMO flow-through fitting. If it is not possible to ensure that the minimum flow velocity is maintained through other means, then the incident flow velocity should be monitored by our flow monitor (1). A suitable fitting (2) for the flow monitor is available (Fig. 8).

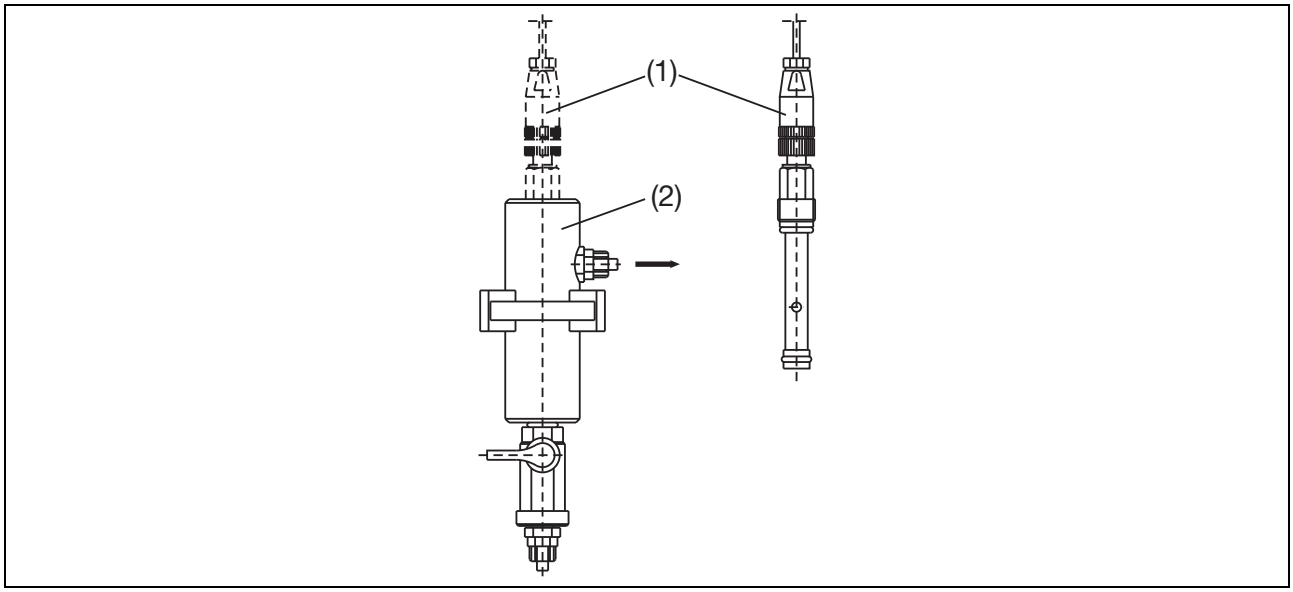

Fig. 8: Flow monitoring with a flow monitor

Protection circuit
If the incident flow velocity falls below the minimum level, the optional flow monitor switches the JUMO dTRANS Az 01 indicator/controller into the “Hold” state and thus prevents an overdose of the disinfectant.

The 4 — 20 mA 2-wire connection is used both to supply the 24 V DC voltage for the cell as to transmit the uncalibrated measurement signal to the evaluation instrument. The cells can also be connected to different indicating/control/recording or PLC systems, as long as they provide the functions previously mentioned.

4.3 General notes on operation

- Measurement can only take place in a suitable flow-through fitting (e.g. JUMO flow-through fitting type 202810/01-102-86, Data Sheet 20.2630).
- The measuring cell should be subjected to as little pressure as possible, with a free outflow for the water being analyzed. If this is not feasible, then the cell can also be operated at a constant pressure up to 1 bar. This makes it easier to arrange a return feed of the water being analyzed.
- Pressure variations must be avoided!
- **No air bubbles** must be allowed to be carried along with the water during pressurized operation.
- During unpressurized operation, where the sample water can run off freely, air bubbles will not cause any problems as long as they do not cover the membrane.
  Air bubbles trapped against the membrane will falsify the measurement signal.
- The transmitter and the connected cell must remain permanently in operation. The cell must not run dry.
- Do not touch the sensitive components.
- Do not screw on the membrane cap until the system is commissioned.

4.4 Faults and malfunctions during measurement with amperometric sensors

Fault/malfunction	Possible cause	Elimination	Preventive measures
(1) Output signal of cell is too low or too high.	Wrong calibration	Repeat calibration	Calibrate cell more frequently, if necessary.
(2) Output signal of cell is too low. Cell cannot be calibrated to the reference value.	Deposit on tip of electrode finger (measurement electrode)	Clean tip of electrode finger.	Shorten service intervals, if necessary.
	Inadequate incident flow onto the measuring cell	Increase the flow.	Monitor minimum flow.
(3) Output signal of cell is too low. Cell cannot be calibrated to the reference value, or decreasing or constant output signal of cell with increasing reference value, or fluctuating signal.	Membrane is destroyed: electrolyte leaks out, sample water leaks in.	Replace the membrane cap.	Avoid damaging the membrane. Do not knock sensor when the membrane cap is screwed on. Avoid any coarse particles or glass splinters in the incident flow.
(4) Output signal of cell is too high. Cell cannot be calibrated to the reference value.	Other oxidation agents are present in the water being analyzed, e.g. ClO_2, O_3	Do not permit addition of these substances. Change water.	Completely remove cleaning and disinfecting agents after use. Disinfectants may only be used individually (no combinations).
(5) Exceptionally slow response of the sensor	Membrane is partially blocked by contamination such as lime or oil. Disinfectant cannot reach the sensor.	Replace the membrane cap. Change the water again before re-using the measurement cell (to remove all contamination).	Take steps to improve the water quality.

5 Sources

5.1 Standards and regulations concerning the measurement of hydrogen peroxide

DIN 38 409	Bestimmung von Wasserstoffperoxid (Determination of hydrogen peroxide)
EN 902	Products for the treatment of water for human consumption – hydrogen peroxide
ISO/DIS 7157	Determination of the hydrogen peroxide concentration – titrimetric method
Ph.Eur.	(European Pharmacopeia), monograph „Hydrogen peroxide: determination of the concentration“

5.2 Literature (German)

H. Römpp, Lexikon Chemie, Thieme Verlag, Stuttgart, 10th Edition, 1997

K.H. Wallhäußer, Praxis der Sterilisation, Desinfektion, Konservierung,
Thieme Verlag, Stuttgart, 5th Edition, 1995

Note
Information on **Workplace safety and general information on hydrogen peroxide** (in German) can be found in the GESTIS materials database of the „Berufsgenossenschaftliche Institut für Arbeitssicherheit“. This information can be downloaded from the Internet at the following address: http://www.hvbg.de

6 Concluding remarks

The contents of this publication represent the present state-of-the-art in measurement technology, standards and legal regulations.

JUMO is continuously developing its products, taking into account present requirements and the latest developments in standards.

It is possible that changes may be made in future by the relevant public bodies in the field of standards and legal regulations concerning information on permissible disinfectants, concentrations and secondary products. So in case of any doubt or discrepancy, the current rules, regulations and standards are to be taken as applicable.

If you have any comments on this publication, your suggestions will be welcome.

Other books and publications are available, including

- Information on high-purity water measurement, FAS 614
- Information on redox voltage measurement, FAS 615
- Information on amperometric measurement of free chlorine, chlorine dioxide and ozone, FAS 619
- Information on pH measurement, FAS 622
- Information on conductivity measurement, FAS 624

In addition, we hold basic courses on various topics and products throughout the year, at our training center in Fulda
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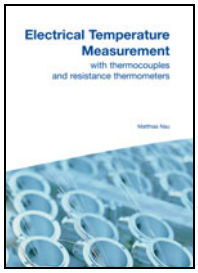
Informative material from JUMO – for beginners and those with some practical experience

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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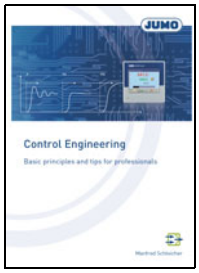

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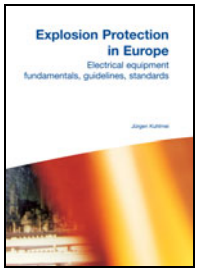

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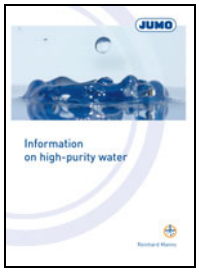

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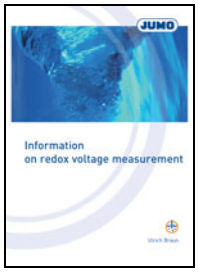

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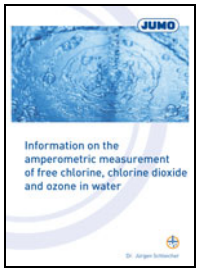

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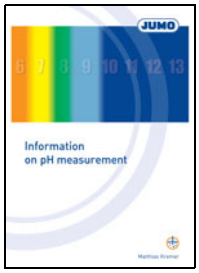

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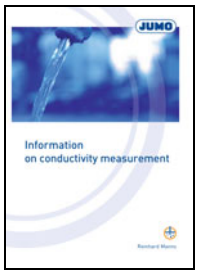

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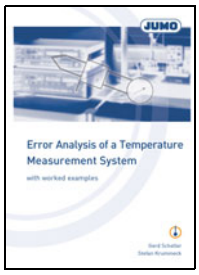

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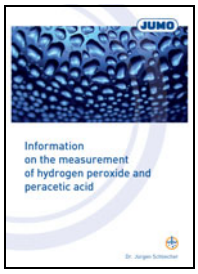

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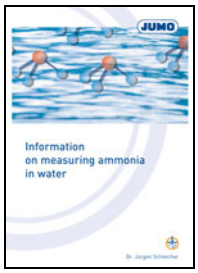

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