

Information on high-purity water

Reinhard Manns

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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

As a manufacturer of measuring systems (transmitter/controllers and sensors) for resistance/conductivity and pH measurement, we are confronted almost every day with the uncertainty prevailing among customers, end users and project planners when it comes to the proper measurement techniques and equipment for high-purity water.

We have written this booklet to provide assistance and information in this field. It is intended to give you a generally understandable background and explanation of the fundamental terminology used in high-purity water measurement, and thus contribute to demystifying the subject. Furthermore, it also presents the procedure that is generally valid (at the time of going to press) for calibrating and testing a high-purity water measuring system, and is currently still firmly based on the American regulations (USP/ASTM).

We are concerned to keep this „Information on high-purity water measurement“ up to date, and therefore appeal to the readers for feedback and the sharing of knowledge and experience. Any comments or contributions to the discussion will be most welcome.

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Dipl.-Ing. (FH) Reinhard Manns

JUMO GmbH & Co. KG
Moritz-Juchheim-Straße 1
36039 Fulda, Germany
Phone: +49 661 6003-0
Fax: +49 661 6003-500
E-mail: analysenmesstechnik@jumo.net
Internet: www.jumo.net

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1.1 Areas of application

High-purity water is needed in a very wide range of production processes, e. g.

- for semiconductor manufacture,
- in the production of medicines, foodstuffs, and cosmetics,
- as a supply to vapor generators,
- in the optical and chemical industries,
- and in other processes that depend on the highest quality (purity) of the water that is used.

1.2 Production

As a rule, ion-exchange and reverse-osmosis plant is used for the production of high-purity water. Various other processing steps may come before or after this plant, depending on the specification that applies to the high-purity water [1].

1.3 Specimen plant

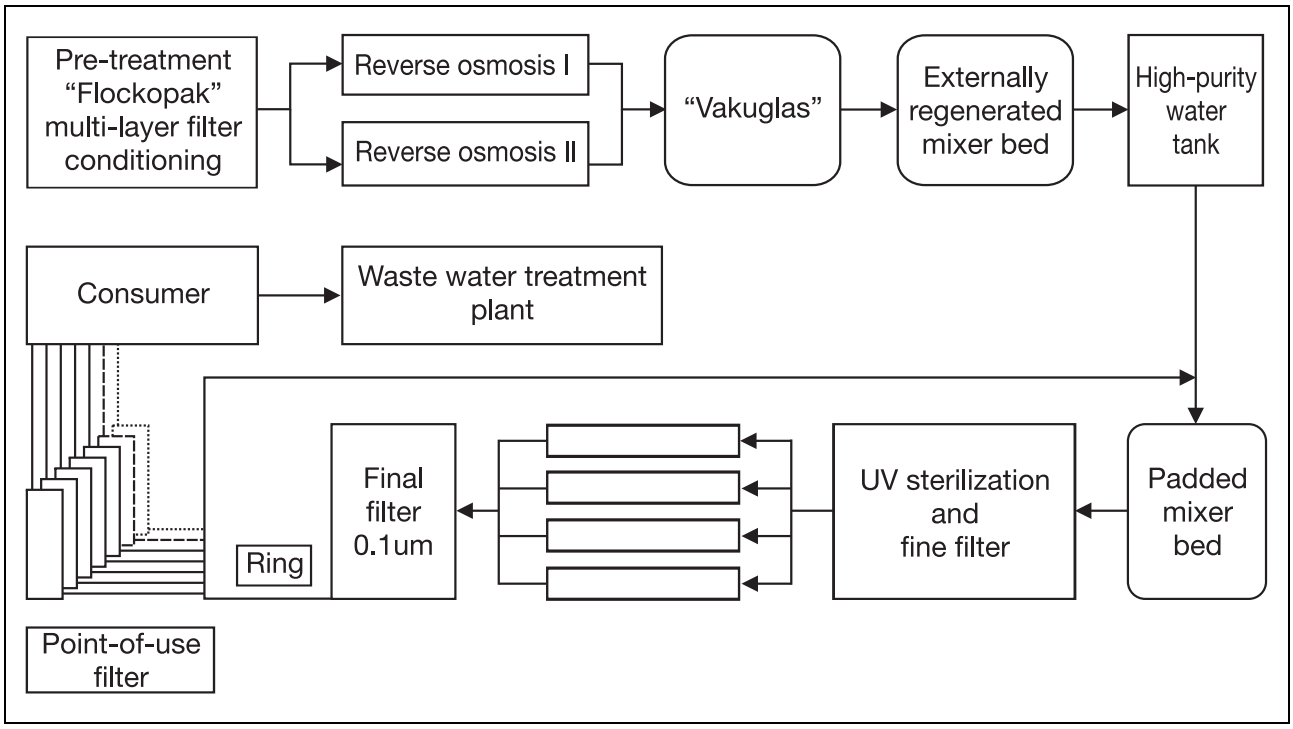


Fig. 1: Production of high-purity water combined with waste-water treatment [1]

1.4 Standards and recommendations

The quality of high-purity water (*ultra pure water*, purified water, water for injection, etc.) is defined in several standards and recommendations, such as the ASTM (**A**merican **S**ociety for **T**esting and **M**aterials), Pharmacopoea Europaea (Ph. Eur.) USP (**U**nited **S**tates **P**harmacopeia) and DIN or ISO standards. Because of the high acceptance level for the US standards and recommendations, these are effectively applied all over the world, or other regulations are used that are derived from them.

Typical conductivity ranges are listed in the following table:
Reference temperature 25 °C

- Plain, untreated water — approx. 300 — 800 µS/cm
- Partially desalinated water — approx. 20 µS/cm
- Pure water (VE-water in Germany) — approx. 2 — 10 µS/cm
- High-purity water — 0.055 — 1 µS/cm

1.5 Testing water quality

The quality of high-purity water can be tested by the following on-line measuring methods (in addition to laboratory analysis): electrical conductivity, **T**otal **O**rganic **C**arbon (TOC) and pH value, as well as particle measurement.

The conductivity reveals impurities that are present in ionized form. These are primarily inorganic ions, such as Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} etc., but also organic ions such as dissociated carbonic acid.

Uncharged organic impurities will not be detected by a conductivity measurement. This omission is covered by the TOC measurement. There are various ways of determining the TOC. All methods are based on oxidizing the organic compounds to carbon dioxide (CO_2) and measuring the CO_2 that is produced.

Acidic or alkaline impurities are detected both through conductivity measurement and the alteration of the pH value.

Particles, which are particularly disturbing in semiconductor production, are determined through means such as laser particle scattering measurement.

2.1 Measurement

A continuous measurement of conductivity can be used for a fast and reliable check of water quality. In general, the conductivity of the medium being measured depends on the number, specific charge, and mobility of the ions. A conductivity sensor measures the sum of all the ions present in the solution.

Measurement is carried out by conductivity sensors that operate on the two-electrode principle. In this application, the electrodes are arranged concentrically, whereby the outer electrode shields the inner one.

Since the electrolytic conductivity is strongly temperature-dependent, the measured value for the liquid under test is usually normalized to the internationally recognized reference temperature of 25 °C (i. e. compensated for temperature). An exception is the special evaluation method as per USP (water conductivity <645>), where the measurement must be uncompensated.

2.2 Components of a measuring system

A complete measuring system for measuring high-purity water consists of:

- A transmitter/controller for high-purity water
- A conductivity cell for high-purity water, with a precisely measured cell constant
- Temperature sensor (usually integrated into the conductivity cell)
- Connecting cable

2.2.1 Operating principle

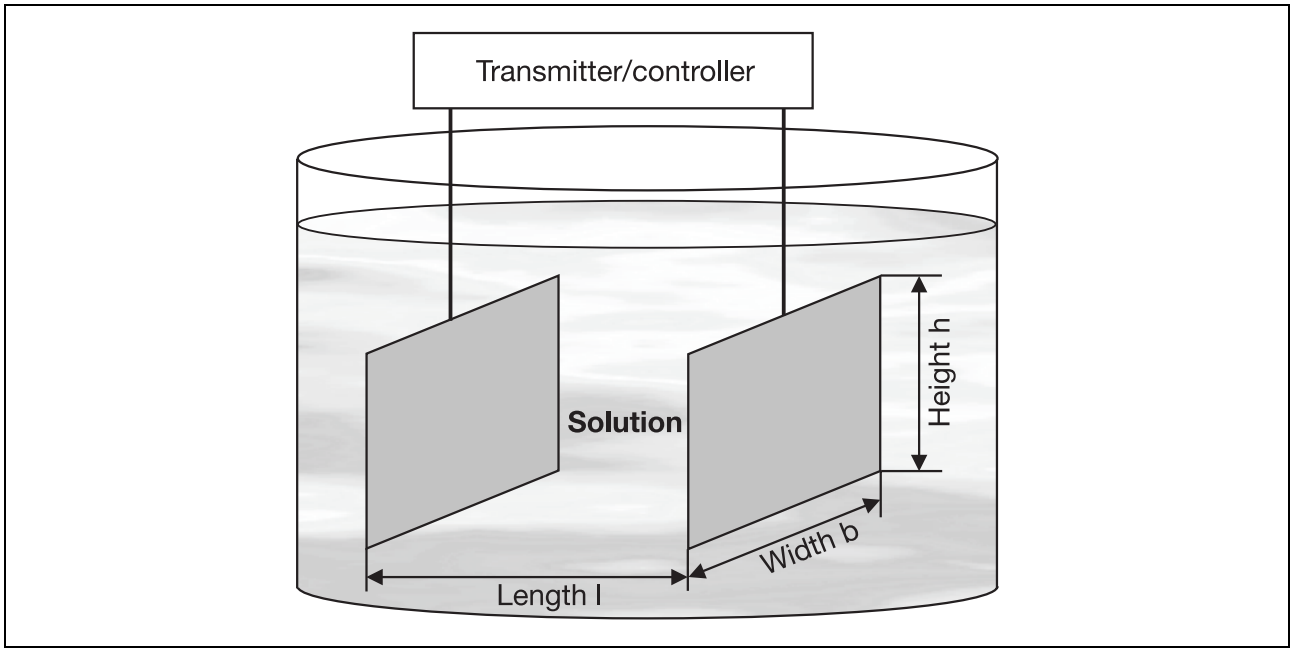


Fig. 2: The principle of measurement is that of conductivity measurement with a 2-electrode conductivity cell

A 2-electrode cell consists of two conductive measuring electrodes (for high-purity water these are made of stainless steel or titanium) that have a particular geometrical arrangement. The geometrical relationship defined by the distance between the cell electrodes (length l) and the effective measuring surface A (width w x height h = area A) is known as the **cell constant K (unit: [1/cm]**).

2 Measuring conductivity

For high-purity water, a cell constant K = 0.01 is required (larger cell constants, e. g. K = 0.1; K = 1.0 etc. mean higher measuring ranges).

Practical cells often have a coaxial design, i.e. the two measuring electrodes are arranged concentrically. In addition, these conductivity cells usually have an integrated temperature sensor to measure the temperature of the medium.

The transmitter/controller applies an AC voltage to the 2-electrode cell. The electrical resistance results in an flow of AC current, which is converted into a conductivity (or resistance) measurement by the transmitter/controller, taking into account the cell constant and the temperature of the medium (if necessary).

2.3 Instrumentation: transmitter/controller



Fig. 3: JUMO dTRANS Rw 01, type 202545



Fig. 4: JUMO AQUIS 500 CR, type 202565



Fig. 5: JUMO ecoTRANS Lf 03, type 202732

2 Measuring conductivity

Background
In the early days of high-purity water measurement, analog circuitry was used, equipped with special adaptations for the conductivity measurement of high-purity water and the associated temperature compensation. These analog transmitter/controllers had to deal with two major problems:

- It is difficult to adjust for the exact cell constant.
- The temperature compensation of the specific resistance or the conductivity of high-purity water cannot function with a constant temperature coefficient (TC). Even more comfortably equipped instruments, that attempt to simulate the temperature coefficient through a non-linear function (NTC compensation) have only limited usability.
  This function is only valid for high-purity water that has no contamination.

State of the art
The present state of the art is the use of microprocessor transmitter/controllers, as described elsewhere. µP technology offers the manufacturers, and through them the users of the measuring instrumentation, a wealth of options.

JUMO transmitter/controllers for high-purity water provide the following options:

- numerical (precise) entry of the cell constant
- temperature compensation as per ASTM D 1125-95
- limit monitoring as per USP (water conductivity <645>)

2.3.1 Temperature compensation

Conductivity of aqueous solutions
The conductivity of aqueous solutions is made up of two components:

- the intrinsic conductivity of water (e. g. 0.055 µS/cm at 25°C) is determined by H_3O^+ and OH^- ions, as a result of autoprotolysis, and
- the conductivity of the additional constituents (e.g. salts, contamination)

Conductivity at varying temperatures
The conductivity of a liquid is heavily temperature-dependent, i. e. the conductivity that is actually measured varies with the temperature.
Depending on the chemical composition of aqueous media, there are different ways in which conductivity may vary with temperature.

Reference temperature
In order to be able to compare measurements with one another, conductivity measurements refer, in most cases, to the internationally used reference temperature of 25 °C.

Temperature compensation
The transmitter/controllers for conductivity or high-purity water must therefore take account of the temperature of the medium:

- manual temperature compensation (TC): The temperature of the medium is entered into a program or set by a potentiometer on the transmitter/controller.
- automatic TC: The actual temperature of the medium is continuously acquired by a temperature sensor (usually integrated into the transmitter/controller) and fed to the transmitter/controller.
- a function must describe the temperature response of the specific water quality (depending on the contamination contained in the high-purity water, for example) as accurately as possible.

Temperature coefficient α (Alpha)
In order for the transmitter/controller to be able to normalize the value actually measured to the equivalent value at 25 °C, a factor termed **temperature coefficient α (Alpha)** must be known.

Alpha is a measure of the per cent alteration of the conductivity per °C, i. e. the unit is [%/ °C].

2.3.1.1 Temperature compensation at higher conductivity levels

In the higher conductivity ranges (from about 10 µS/cm), the additional constituents of the water are the determining factors for conductivity and the temperature dependence. The intrinsic conductivity of the water is masked by the conductivity and characteristics of the other constituents.

For the general run of aqueous media, the value of Alpha is typically in the range 0 — 5 %/°C.
A linear dependency is assumed.
In order to obtain correct measurements, the transmitter/controller must offer the facility of adjusting the Alpha value.

Note
Instruments with a fixed, preset Alpha value – such as are, unfortunately, still being offered by cheap sources – should not be used nowadays. They can only produce a relative measurement.

2.3.1.2 Characteristics of high-purity water

With high-purity water, the relationships are **non**-linear. The Alpha value can be up to 20 %/°C. In this case, the intrinsic conductivity of the water is decisive.

Industrial production of high-purity water
In most cases, industrial production of high-purity water involves multi-stage processing that often makes use of reverse osmosis and ion exchange as processing methods. These nearly always employ ion exchangers consisting of cation and anion exchange resins. When exhausted (i.e. overloaded), these resins will start to discharge sodium and/or chlorine ions, i.e. common salt (sodium chloride), into the high-purity water, which can be taken into account when setting the temperature compensation on JUMO instruments.

Effect of contamination
JUMO transmitter/controllers for high-purity water not only take account of the non-linear temperature dependency of high-purity water, but also the effects of contamination by traces of hydrochloric acid, sodium hydroxide or sodium chloride (described in ASTM D 1125-95, valid for JUMO instrument types JUMO AQUIS 500 CR, JUMO dTRANS Rw 01 and JUMO ecoTRANS Lf 03).

ASTM D 1125-95 and ASTM D 5391-99 (**A**merican **S**ociety for **T**esting and **M**aterials)
In its Standard Test and Analysis Procedures, this organization also lays down methods for determining the electrolytic conductivity of water and high-purity water: (Designation) D 1125-95. This treatise presents the variations of high-purity water measurements depending on the temperature and various types of contamination.

2.3.1.3 Uncompensated operation

Uncompensated indication of conductivity
For some applications, it may be necessary to display the uncompensated value of the conductivity (JUMO instrument types JUMO AQUIS 500 CR, JUMO dTRANS Rw 01 and JUMO ecoTRANS Lf 03 provide this facility). This could be the case if none of the special compensations mentioned above is suitable, or if individual (user's own) conductivity tables are to be used.

2.3.2 USP contact

USP (**U**nited **S**tates **P**harmacopeia Convention)
The USP publishes (amongst other things) rules and recommendations for the pharmaceutical sector.

These rules form a world-wide quasi-standard. European rules and standards are frequently based on these collections of rules and regulations.

The publication *USP* Physical test method (water conductivity <645>) covers measurement of the conductivity of high-purity water.

USP contact
With the JUMO AQUIS 500 CR, JUMO dTRANS Rw 01 and JUMO ecoTRANS Lf 03 it is possible to monitor the quality of water on-line, according to the method given in USP 25 Stage 1.

USP 25 includes a table that shows a limit for the conductivity according to the temperature. If the conductivity remains below the limit, then the high-purity water fulfills the requirements of USP.

Note
The temperature compensation must be switched off when this monitoring is being used.

Temperature °C	max. conductivity in µS/cm (uncompensated)	Temperature °C	max. conductivity in µS/cm (uncompensated)
0	0.6	55	2.1
5	0.8	60	2.2
10	0.9	65	2.4
15	1.0	70	2.5
20	1.1	75	2.7
25	1.3	80	2.7
30	1.4	85	2.7
35	1.5	90	2.7
40	1.7	95	2.9
45	1.8	100	3.1
50	1.9		

Table 1: Extract from USP 25

When this table is used, it is possible to monitor the conductivity without applying compensation. If the conductivity exceeds the value for the corresponding temperature, the configured contact will switch.

The JUMO transmitter/controller dTRANS Rw 01
offers the following additional facility as standard:
If the situation is such that the process temperature happens to vary around a switching point, a temperature hysteresis can be activated which ensures that the monitoring is always on the safe side.
In detail, this means that if, for instance, the temperature varies between 55.5 °C and 54.3 °C, then the limit value for the monitoring (1.9 µS/cm) is valid throughout (the temperature hysteresis here is 1 °C, to raise the switching point for the lower conductivity value by 1 °C, covering the higher value). This measure can stop the installation oscillating (thus higher plant reliability, reduced costs).

2.3.3 Ph. Eur. limits

The European Pharmacopeia (Ph. Eur.) permits a wider tolerance range for the conductivity of purified water than is given by USP 25. A maximum of 4.3 µS/cm is allowed at 20 °C. USP, on the other hand, only permits 1.1 µS/cm at 20 °C as the upper limit for the conductivity of purified water.

Temperature °C	conductivity in µS/cm	Temperature °C	conductivity in µS/cm
0	2.4	60	8.1
10	3.6	70	9.1
20	4.3	75	9.7
25	5.1	80	9.7
30	5.4	90	9.7
40	6.5	100	10.2
50	7.1		

Table 2: Ph. Eur. limits

Water for injection, WFI, as well as highly purified water, HPW, have to satisfy more stringent requirements. In this case, both Ph. Eur. and USP, allow a maximum of 1.1 µS/cm at 20 °C.

	Water quality in accordance with table	JUMO AQUIS	JUMO dTRANS Rw	JUMO ecoTRANS Lf 03
PW (USP)	1 (page 12)	yes	yes	yes
HPW (Ph. Eur.)	1	yes	yes	yes
WFI (Ph. Eur.)	1	yes	yes	yes
WFI (USP)	1	yes	yes	yes
PW (Ph. Eur.)	2 (page 13)	yes	yes	no

Table 3: The user of JUMO devices can select water qualities indicated above

PW = „Purified Water“
HPW = „Highly purified water“, „Aqua valde purificata“
WFI = „Water for injection“, „Aqua ad iniectabilia“

2.3.4 Quality assurance in the manufacture of transmitter/controllers

JUMO is certified to ISO 9001.

All JUMO test installations and items of equipment are traceable to national and international standards.

The most modern production methods
The transmitter/controllers are based as far as possible on SMD modules that are manufactured on automated production lines. This method of production ensures a very high and consistent quality level.

The transmitter/controllers are adjusted electrically with precision resistors.

And JUMO transmitter/controllers for high-purity water are also built using the latest microprocessor technology.

USP requirements	Fulfilled by JUMO?
Instrument calibration using traceable precision resistors	yes
Measurement resolution better than 0.1 µS/cm	yes
Instrument linearity better than 0.1 µS/cm	yes
Automatic temperature compensation in the transmitter/controller	yes
Reference temperature in the instrument must be 25 °C	yes
Accuracy of the temperature measurement better than ±2°C	yes

Table 4: Requirements of USP (water conductivity <645>) for the transmitter/controller or the factory adjustment of the same

For most aspects, JUMO transmitter/controller not only meet but exceed the minimum!

2.3.5 Test certificates

Basics
The use of measuring instrumentation in the areas of quality assurance or pharmacy leads to increasing uncertainty of the users of the equipment with regard to the requirement for „certificates“.

No test certificate can make a measurement „more precise“ or „more reliable“. Test certificates are basically just statements of the quality at the time of testing. Certification to ISO 9001 provides a fundamental assurance of quality. It means that the supplier must maintain the technical data as given in the data sheets.

So before jumping in and demanding extra certificates that will only be put on one side and never needed again, it is advisable to be quite clear as to what is really required. Since some certificates cost extra, and may delay delivery, this point should be looked at even more closely.

Test certificates for transmitter/controllers
The transmitter/controllers can be delivered with the following test certificates:

- Factory certificate 2.1 to EN 10 204/DIN 50 049 - free of charge
- Factory certificate 2.2 to EN 10 204/DIN 50 049 - charged according to effort
- Acceptance certificate 3.1B to EN 10 204/DIN 50 049 - charged according to effort
  (3.1B certificates are material test certificates, not normally required for transmitter/controllers)

2.4 Instrumentation: Measuring cells



Fig. 6: Two-electrode conductivity cells

Two-electrode conductivity cells are used for measuring high-purity water. In these cells, the electrodes are arranged concentrically, whereby the outer electrode shields the inner one.

2.4.1 Cell constant

The geometrical factor described in section 2.2 *„Components of a measuring system“*, the **cell constant K**, is particularly important for the measurement of high-purity water.

Production tolerances mean that the cell constant for ordinary commercial cells varies by up to to ±10 %. At the first glance, this does not seem to be enormously inaccurate, but a wrongly set temperature coefficient can cause far greater errors in the measurement.

In accordance with USP, the cell constant must be known with an accuracy of ±2 %. JUMO measuring cells can be supplied with an ASTM test certificate, in which the precise cell constant is certified.

Modern types of transmitter provide numerous options (such as automatic determination of the cell constant, calibration by means of test solutions etc.) to enable an individual calibration of the conductivity cell. Temperature, temperature coefficient and cell constant are thus taken into account.

Characteristics of high-purity water
If the ASTM temperature compensation is used (see section 2.3.1.2 *„Characteristics of high-purity water“*) then the possible measurement error caused by a wrongly set temperature coefficient is eliminated. The major influence on measurement error is then that resulting from an imprecise cell constant.

Conductivity cells for measuring high-purity water can also have deviations from their nominal cell constant K = 0.01.

Unfortunately, there are practically no test or calibration solutions available for the high-purity water range, i. e. below 10 µS/cm.

Liquids with such a low conductivity do not provide stable reference values, since they rapidly absorb CO_2 from the atmosphere and become unstable.

Preparing a measurement installation for high-purity water
For high-purity water, it is therefore necessary to use a cell that has a precisely measured cell constant. The manufacturer delivers such cells with a certificate, for instance the ASTM test certificate, which gives the cell constant quite precisely, to an accuracy of several decimal places. So it is only necessary to enter this precise cell constant into the transmitter/controller during commissioning. The high-purity water measuring installation is thereby calibrated and ready for measurement.

Regulations
The procedure for determining the precise cell constant in the factory is laid down in the ASTM documentation of rules and regulations. European regulations are not yet available.

2.4.2 Factory procedure for determination of the cell constant as per ASTM D 5391-99 and ASTM D 1125-95

The cell constant is measured by using a comparison method. The liquid that is used for this purpose has a conductivity in the range 5 — 10µS/cm.

ASTM D 5391-99 works on the premise that the cell constant that is measured in this range is also valid for lower values of conductivity (i. e. the high-purity water range).

Setup
The equipment installation consists of a high-purity water circulation, a reference conductivity measurement, and the cell to be measured. This is connected to a laboratory conductivity transmitter/controller. When a stable value of conductivity has been reached (checked by the reference conductivity measurement, which is made without temperature compensation) the laboratory conductivity transmitter/controller is used to determine the cell constant for the conductivity cell under test.
USP (water conductivity <645>) requires that the cell constant is determined to an accuracy of ±2 %.

JUMO instruments meet this requirement.

Results
The results of the measurement are entered in the appropriate test records with other relevant data. The test installations and items of equipment are traceable to national and international standards.

2.4.3 Materials and process connections

The materials used for the high-purity water measuring cell depend on the applications requirements and the specific situation at the measurement site. The same applies to the process connection for the measuring cell.

The following factors influence the selection:

- Process pressure
- Temperature of the medium
- Material of the piping in which the measuring cell is to be installed
- Hygienic requirements

Standard materials for measuring cells are stainless steels, such as 1.4435; AISI316L or DIN 1.4571. Titanium is recommended as the electrode material for ultra-pure water.

JUMO also offers options for the process connections:

- Screw-in DIN or NPT pipe threads in various sizes
- (Tri-) Clamp
- Milk cone
- Customer-specific

For demanding hygienic specifications, versions are available in polished stainless steel with an <0.8µm surface finish.

2.4.4 Quality assurance in the manufacture of measuring cells

JUMO is certified to ISO 9001.

All JUMO test installations and items of equipment are traceable to national and international standards.

JUMO has a very deep production, i.e. even the basic components of the cells are manufactured in-house on the most modern CNC machines. This ensures a consistently high level of quality. And every cell is subjected to individual testing to achieve the highest quality possible.

JUMO conductivity cells for measuring high-purity water are used in sensitive areas, such as food technology and pharmacy and, of course, they fulfill all the requirements of the market and the leading organizations:

- USP marking of cell constant with ±2 % accuracy
- Materials as per EHEDG (**E**uropean **H**ygienic **E**quipment **D**esign **G**roup):
  such as DIN No. 1.4404, DIN No. 1.4435, AISI316L, DIN No. 1.4571
- Surface finish as per EHEDG (**E**uropean **H**ygienic **E**quipment **D**esign **G**roup): Ra <= 0.8µm
- Sealing and body material approved by FDA (**F**ood and **D**rug **A**dministration (American foodstuff regulatory authority)) and/or BGA (**B**undes**g**esundheits**a**mt (former designation)):
  e. g. EPDM, PVDF

All these points are met by JUMO conductivity cells, or available as options.

2.4.5 Test certificates

Remarks on test certificates see section 2.3.5 *„Test certificates“*.

Test certificates for measuring cells
The following test certificates can be specifically ordered for measuring cells:

- ASTM test certificate - Surcharge: see current price list
  Exact determination of cell constant
- Factory certificate 2.1 to EN 10 204/DIN 50 049 - free of charge
- Factory certificate 2.2 to EN 10 204/DIN 50 049 - charged according to effort
- Acceptance certificate 3.1B to EN 10 204/DIN 50 049 - charged according to effort
  (e. g. material confirmation: stainless steel 1.4571, confirmation of surface finish etc.)

2 Measuring conductivity

2.5 Instrumentation: cable material/connecting cable

Thanks to the modern, precise measurement technology of microprocessor transmitter/controllers, there are only a few points to be considered when selecting cable material, such as:

- The cable material that is used is a shielded control cable type.
- Cables lengths up to about 50 meters (depending on the local conditions) do not present any problem for modern µP-based instruments such as the types JUMO AQUIS 500 CR, JUMO dTRANS Rw 01 and JUMO ecoTRANS Lf 03.
- Cables should always be routed directly, i. e. avoid using terminal boxes, intermediate connectors, or supplementary cable extensions.

Suitable JUMO types 2990-9 (length specified) - 0

2.6 On-site test options

Manufacturers of measurement and control instrumentation are frequently asked about the reliability of continuous measurement. For high-purity water in particular, comparative measurements are often only feasible through laboratory analysis.

The following options are available to the plant operator on site:

2.6.1 Testing the transmitter/controller

The transmitter/controller can be checked by using precision resistors.
However, this is done on the assumption that the transmitter/controller will not have lost its precision (as adjusted) in normal circumstances.

2.6.2 New determination of the cell constant

Since the measuring cell is exposed to the medium being measured and its constituents, it makes sense to check it at regular intervals (by determining the cell constant).

2.6.3 Test interval

The interval between tests can be laid down by the plant user or legal requirements. During this procedure, the transmitter/controller is adjusted to match the new (altered) cell constant.

2.6.4 Comparative measurement

A comparative measurement with a reference instrument can be used to make a fresh determination of the cell constant of the high-purity water measuring cell.
In this case, care must be taken that the temperature compensation is switched off for both instruments (the JUMO instrument and the reference instrument) i. e. the temperature coefficient is set to 0 %/°C.

2.6.5 Factory measurement

If the user does not have the appropriate test and measurement equipment available, then the cell constant can also be determined by the manufacturer (JUMO).

For such situations, it may be a good idea to have two calibrated measuring cells available on site, to avoid down-times.

3 Total Organic Carbon - TOC

3.1 General

The measurement of the electrical conductivity of high-purity water is supplemented by another measurement method that detects (non-ionic) organic contamination.

Although JUMO does not supply TOC equipment, we would like to provide a brief introduction to this method of measuring high-purity water at this point.

The TOC method is included in many regulations on high-purity water. TOC values are given in pharmacopeia such as the USP, Ph. Eur.), and are cited in DIN and ASTM standards.

Terms and abbreviations
Several related terms and abbreviations are used in connection with TOC regulations:

- TC (total carbon)
- TOC (total organic carbon)
- TIC (total inorganic carbon)
- DOC (dissolved organic carbon)
- VOC (volatile organic carbon)

They are linked as follows:

$$TC = TIC + TOC$$

3.2 TOC principle of measurement

In general, a TOC measurement involves oxidizing the organic material to carbon dioxide, and then determining the carbon dioxide content. The CO_2 determination is carried out through infra-red spectroscopy or conductometry.
In the first case, the carbon dioxide can be selectively detected by the absorption in the near infra-red (NIR) spectrum.
In the second case, the carbon dioxide is measured by the increase in electrical conductivity of the sample solution.

Method
Various methods can be applied to oxidize the organic constituents to carbon dioxide.

- Thermal oxidation with oxygen or artificial air, at temperatures up to 1200 °C, possibly using catalysts such as platinum.
- Wet-chemical oxidation, using a chemical such as sodium peroxodisulfate, potassium dichromate or potassium permanganate.
- Oxidation through UV radiation (disintegration), possibly with added oxygen or a chemical oxidation agent.

Areas of application
The last of these three methods is frequently used as an on-line method for determining the TOC of high-purity water. The two other methods, on the other hand, are most frequently applied in areas where higher TOC values have to be measured, such as for waste water.

3.2.1 Differentiating between TIC and TOC

Direct or extraction methods
TIC has to been determined before TOC, by acidification and blowing out, i. e. the physically dissolved CO_2 or hydrogen carbonate/carbonates are driven out in the form of carbon dioxide. This step can also vaporize volatile organic compounds (VOCs), such as benzole, haloforms etc.

Indirect methods
TC and TIC are determined in separate tests. The TOC is then derived as the difference between TC and TIC.

The first method is frequently used for high-purity water, since here it may be assumed that no VOC constituents are present.

3.3 TOC in high-purity water in the pharmacopeia: USP and Ph. Eur.

TOC determination in high-purity water is described in USP and Ph. Eur., whereby the monography in Ph. Eur. conforms to USP in almost all aspects. No particular method is specified for oxidation or determination.

The suitability of a method must be established through a „system suitability test“: Here the system is tested with a substance that is known to be difficult to oxidize (1,4-benzochinone) in a comparison with an easily oxidizable reference substance (saccharose), whereby the blank value of the water is taken into consideration. A further requirement in the Ph. Eur. and USP pharmacopeia is that the measuring system is able to distinguish between organic and anorganic carbon-bearing compounds, and has a detection threshold for TOC that is below 0.05 mg/liter.

Both pharmacopeia specify an upper limit of 0.5 mg C/liter (500 parts per billion) for TOC.

4 pH measurement of high-purity water

A pH measurement is also specified for many high-purity water applications. Carrying out a pH measurement for high-purity water presents problems in measurement technology, mostly resulting from the low conductivity (low ionic concentration level) of the high-purity water. These problems become larger as the conductivity becomes smaller.

Diaphragm resistance
A major part of the problem with pH measurement for high-purity water arises at the diaphragm of the reference electrode. DIN 19 264 places an upper limit of 5kΩ on the diaphragm resistance, so that the voltage drop across the diaphragm of the reference electrode remains as small as possible.

The diaphragm resistance is further increased by the poor conduction of the high-purity water that diffuses into the diaphragm, in spite of the electrolyte flow in the opposite direction. In order to prevent the diaphragm resistance becoming too high, because of the water under test diffusing back in, it is necessary to operate with a relatively high rate of outwards flow of the reference electrolyte. For this reason, electrodes that have a solidified reference electrolyte should not be used.

Dispersion resistance
The dispersion resistance makes itself felt immediately after the diaphragm of the reference electrode, where the electrolytic conduction has to be transferred to the ions contained in the high-purity water. At this point, the reference electrolyte entering the water under test is at least partially responsible for conduction. The dispersion resistance varies according to the type and area of the diaphragm that is used. As a rule, a ground diaphragm is the solution that creates the lowest resistance.

Diaphragm	Diameter	Diffusion resistance
Ceramic	0.6mm	6600kΩ
Ceramic	1.0mm	4000kΩ
Ceramic	3x 1.0mm	1300kΩ
Normal grinding	NS 7/17mm	800kΩ

Table 5: Galster [2] gives the following values for the diffusion resistance of various diaphragms in completely desalinated water

In addition to the favorable diffusion resistance, a ground diaphragm has the advantage of being less dependent on the incident flow than other types of diaphragm. The incident flow should vary as little as possible during the measurement.

Diffusion potential
Another problem with pH measurement of high-purity water is the diffusion potential, which arises on the interface where the high-purity water and the electrolyte solution come into contact. The diffusion potential is caused by the different diffusion velocities of the ions involved in the charge transport, and is added in to the total potential. In the diffusion of the ions from the side with the concentrated reference electrolyte across the side with the high-purity water, the anions and cations do not have the same velocity: one type can, so to speak „overtake“ the other. This leads to a separation of the charge and thus the appearance of the diffusion potential. The charge separation acts so as to oppose the electrical field that is built up. Eventually, a balance is achieved.

KCl is mostly used as the reference electrolyte, since for this substance the diffusion velocities of anions and cations are very similar. Nevertheless, a diffusion potential also appears in this case.

4 pH measurement of high-purity water

The magnitude of the diffusion potential that is built up can be calculated, according to Henderson [3]. The Henderson equation can be used to show that, in the case of high-purity water, the magnitude of the diffusion potential is reduced as the concentration of the reference electrolyte falls [4]. However, it is not possible to simply reduce the concentration of the reference electrolyte at will, as this leads to errors in the calibration using buffer solutions. So one usually makes a compromise, using, for instance, 1 mol/liter KCl as a reference electrolyte. In addition, avoiding the KCl concentration falling too low also reduces the risk of the diaphragm becoming clogged with precipitated AgCl. AgCl is more soluble in highly concentrated KCl solutions than in less concentrated solutions, and can therefore be precipitated when the reference electrolyte is diluted by the high-purity water penetrating the diaphragm.

Shielding and grounding
One effect of the low conductivity of high-purity water is that electrostatic charge can only disperse slowly, so **good** shielding and grounding is recommended. All ground leads should be brought together at a central point, and earthed from this point only.

Weak buffer
High-purity water is naturally only weakly buffered, or not at all. As a result, even the slightest traces of substances that influence the pH value, from the atmosphere or parts of the installation, such as atmospheric CO_2 or alkalis from the glass, will cause a large change in the pH of the high-purity water. The pH of high-purity water will, for instance, fall from 7 to a value of about 5.4, if the water is saturated with air [4]. Even a 1 % saturation with air will reduce the pH of the high-purity water to 6.4. So it is always necessary to operate with a closed flow-through fitting in order to exclude atmospheric carbon dioxide. It is best to use an properly earthed metal fitting.

Additives
It is sometimes recommended that you add neutral salts such as KCl to the high-purity water, to increase its conductivity and thus make it easier to carry out the pH measurement. USP 25, for example, suggests (for various pre-packed water qualities, such as Sterile Purified Water, Bacteriostatic Water for Injection, Sterile Water for Inhalation, Sterile Water for Injection) adding 0.3 ml of saturated KCl solution per 100 ml of test solution and then measuring the pH. But the source literature [2] advises against this, since the alteration in the concentration of ions or impurities introduced into the weakly buffered water can have a substantial influence on the pH.

Buffer solutions
The less concentrated standard buffer solutions as per DIN 19 266 should be used for the calibration of electrodes to be applied with-purity water, rather than the technical buffer solutions of DIN 19 267. This reduces the „memory effect“ in the diaphragm of the reference electrode, that is caused by the layering of the reference electrolyte/high-purity water/buffer solution, and speeds up the recovery. The use of standard buffer solutions with a lower ionic concentration also has the advantage that the diffusion potentials that arise on the diaphragm, between the reference electrolyte and the high-purity water or between the reference electrolyte and the standard buffer solution, are closer together. So the error that results from the assumption that the diffusion potentials are the same for the calibration and for the actual measurement will be reduced.

4.1 Instrumentation for pH measurement

If an on-line pH measurement is required for water with a low conductivity, then we recommend using JUMO instruments, to minimize the problems that inevitably arise with this type of measurement (see section 4).

- Ground combination electrode with liquid reference electrolyte (type 2GE-2-D-KCl-U-ground) used together with a KCl reservoir (Sales No. 00060254)



Fig. 6: Ground combination electrode with KCl reservoir

- Transmitter/controller for pH (type JUMO dTRANS pH 01)



Fig. 7: Transmitter/controller for pH - JUMO dTRANS pH 01

4 pH measurement of high-purity water

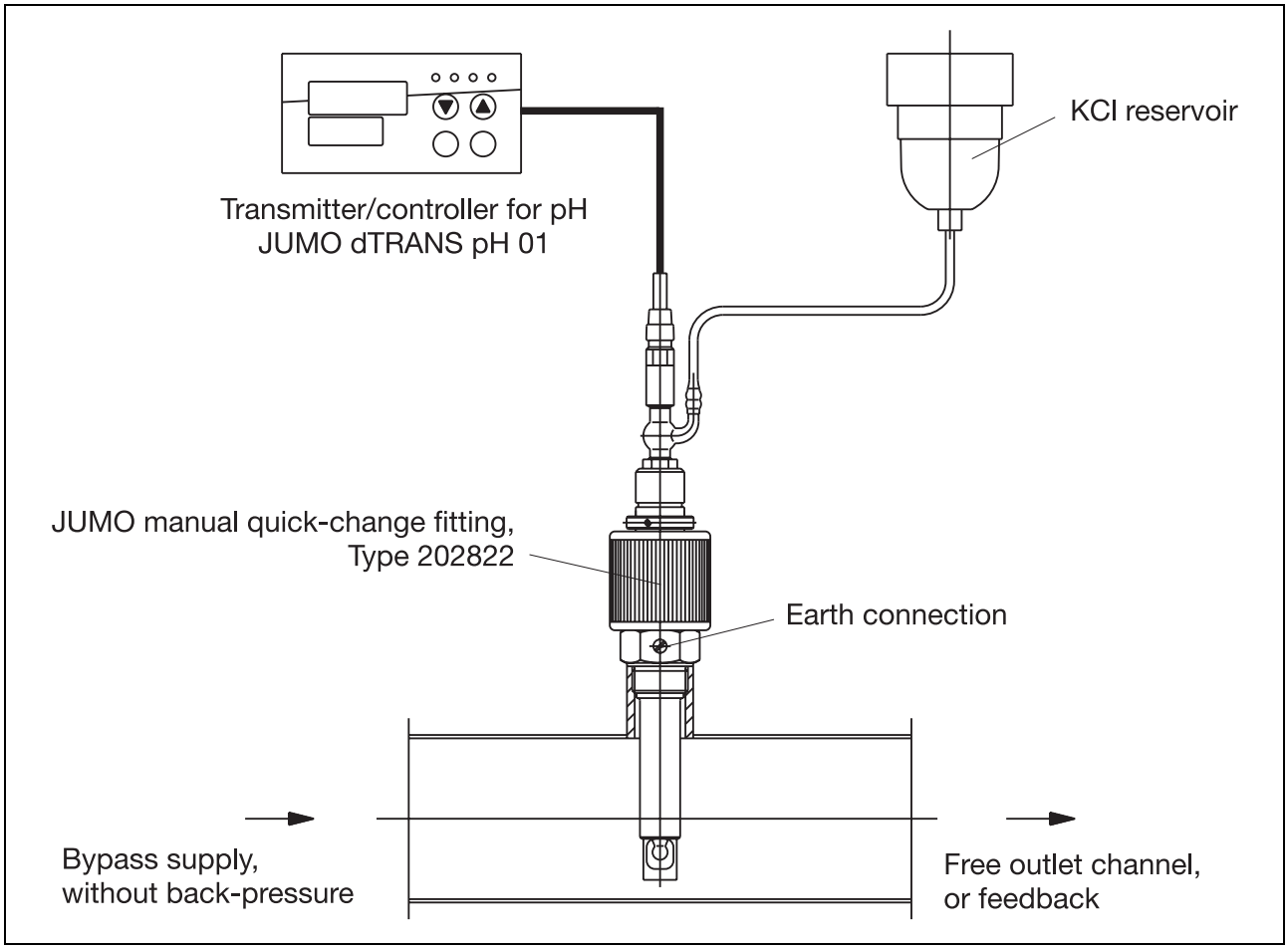


Fig. 8: Example of a set-up for measuring high-purity water

The earthing/grounding of the metal fitting must be joined together with any other grounding leads that are present.

The reference electrolyte used should be 1 mol/liter KCl instead of the usual 3 mol/liter KCl.

For calibration, the preferred buffer solution is a diluted standard buffer solution as per DIN 19 266 instead of a technical buffer solution to DIN 19 267.

The on-line pH measurement is best made on a free-flowing outlet, to avoid pressure fluctuations causing problems with the diaphragm.

The intentional leakage of reference electrolyte through the ground diaphragm means that the out-flowing sample water is contaminated by the KCl. A decision must be made whether to feed this water back into the high-purity water stream, to pass it through a processing stage (ion-exchanger or reverse-osmosis) or discharge it as waste.

5 Points to be observed in handling high-purity water

- In order to maintain the required quality level, the high-purity water must be kept continuously in motion.
- The entire system must be as free of dead space as possible.
- Depending on the installation, the measurement may be sensitive to the incident flow. This must be taken into account in choosing the mounting position.
- High-purity water attacks CrNi steel. Corrosion loss rate is from 0.01 to 0.05 µm/year. Titanium is a possible substitute.
- The change in conductivity and pH, if high-purity water is exposed to the atmosphere for 24 hours is:

Conductivity increase	from 0.05 µS/cm up to 3 to 4 µS/cm!
pH reduction	from pH 7 to pH 5.5 — 5.2!

These changes are caused by the formation of hydrogen carbonate ions resulting from the absorption of CO_2 from the air.

5 Points to be observed in handling high-purity water

6.1 Standards, pharmacopeia, regulations

6.1.1 ASTM-Standards

- ASTM D 1125
  Standard Test Methods for Electrical Conductivity and Resistivity of Water
- ASTM D 1129
  Terminology Relating to Water
- ASTM D 1192
  Specification for Equipment for Sampling Water and Steam
- ASTM D 1193
  Standard Specification for Reagent Water
- ASTM D 1293
  Standard Test Methods for pH of Water
- ASTM D 2777
  Standard Practice for Determination of Precision and Bias of Applicable Test Methods of Committee Dd-19 on Water
- ASTM D 3370
  Practices for Sampling Water
- ASTM D 3864
  Practice for Continual On-Line Monitoring Systems for Water Analysis
- ASTM D 4453
  Standard Practice for Handling Ultra-Pure Water Samples
- ASTM D 4519
  Standard Test Method for On-Line Determination of Anions and Carbon Dioxide in High Purity Water by Cation Exchange and Degassed Cation Conductivity
- ASTM D 5127
  Standard Guide for Ultra Pure Water Used in the Electronics and Semiconductor Industry
- ASTM D 5128
  Standard Test Method for On-Line pH Measurement of Water of Low Conductivity
- ASTM D 5391
  Standard Test Method for Electrical Conductivity and Resistivity of a Flowing High Purity Water Sample
- ASTM D 5464
  Standard Test Methods for pH Measurement of Water of Low Conductivity
- ASTM D 6569
  Standard Test Method for On-Line Measurement of pH
- ASTM E70-97
  Standard Test Method for pH of Aqueous Solutions With the Glas Electrode

6 Source literature

TOC

- ASTM D 2579
  Standard Test Method for Total Organic Carbon in Water

- ASTM D 4779
  Standard Test Method for Total, Organic, and Inorganic Carbon in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection

- ASTM D 4839
  Standard Test Method for Total Carbon and Organic Carbon in Water by Ultraviolet, or Persulfate Oxidation, or Both, and Infrared Detection

- ASTM D 5173
  Standard Test Method for On-line Monitoring of Carbon Compounds in Water by Chemical Oxidation, by UV Light Oxidation, by Both or by High Temperature Combustion Followed by Gas Phase NDIR or by Electrolytic Conductivity

- ASTM D 5997
  Standard Test Method for On-Line Monitoring of Total Carbon, Inorganic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection

- ASTM D 6317
  Standard Test Method for Low Level Determination of Total Carbon, Inorganic Carbon and Organic Carbon in Water by Ultraviolet, Persulfate Oxidation, and Membrane Conductivity Detection

6.1.2 Pharmacopeia

Ph. EUR.

Methods:

- 2.2.3 - pH value - potentiometric methods
- 2.2.44 - Total organic carbon in water for pharmaceutical purposes

Monographs:

- Purified water
- Highly purified water
- Water for injection purposes

USP

Physical Tests

- <643> - Total Organic Carbon
- <645> - Water Conductivity

Official Monographs:

- Water for Injection
- Bacteriostatic Water for Injection
- Sterile Water for Inhalation
- Sterile Water for Injection
- Sterile Water for Irrigation
- Purified Water
- Sterile Purified Water

6.1.3 VDI-Richtlinien (VDI Regulations - documentation in German)

- VDI 2083 Blatt 9
  Qualität, Erzeugung und Verteilung von Reinstwasser (Entwurf)
- VDI 3870 Blatt 10
  Messen von Regeninhaltsstoffen – Messen des pH-Wertes in Regenwasser

6 Source literature

6.1.4 DIN/ISO/EN standards (mostly German)

- DIN ISO 3696 (ISO 3696)
  Water for analytical laboratory use

- DIN EN 1484
  Wasseranalytik – Anleitungen zur Bestimmung des gesamten organischen Kohlenstoffs (TOC) und des gelösten organischen Kohlenstoffs (DOC)

- DIN EN 27 888
  Wasserbeschaffenheit – Bestimmung der elektrischen Leitfähigkeit (= ISO 7888)

- ISO 8245
  Water quality – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

- ISO 10 523
  Water quality – Determination of pH

- DIN 19 260
  pH-Messung – Allgemeine Begriffe

- DIN 19 261
  pH-Messung – Messverfahren mit Verwendung potentiometrischer Zellen – Begriffe

- DIN 19 262
  Steckbuchse und Stecker geschirmt für pH-Elektroden

- DIN 19 263 (Entwurf)
  pH-Messung - pH-Messketten

- DIN 19 264
  pH-Messung; Bezugselektroden

- DIN 19 265
  pH-/Redox-Messung - pH-/Redox-Messumformer-Anforderungen

- DIN 19 266
  pH-Messung – Referenzpufferlösungen zur Kalibrierung von Messeinrichtungen

- DIN 19 267
  pH-Messung; Technische Pufferlösungen, vorzugsweise zur Eichung von technischen pH-Meßanlagen

- DIN 19 268 (Entwurf)
  pH-Messung von wässrigen Lösungen mit pH-Messketten, mit pH-Glaselektroden und Abschätzung der Messunsicherheit

- DIN 38 404-5
  Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Physikalische und physikalisch-chemische Kenngrößen (Gruppe C); Bestimmung des pH-Wertes (C5)

- EHEDG, 1995

- JUMO data sheets
  T 20.2501, T 20.2525, T 20.2530, T 20.2545, T 20.2810, T 20.2900, T 20.2921

6.2 Literature (German)

[1] K. Marquardt, Rein- und Reinstwasseraufbereitung, Expert Verlag, Renningen Malmsheim 1994

[2] H. Galster, pH-Messung, VCH Verlagsgesellschaft mbH, Weinheim 1990

[3] P. Henderson, Z. Phys. Chemie 59, 118 – 127 (1907)

[4] H. Galster, VGB Kraftwerkstechnik 59, 885 – 889 (1979)

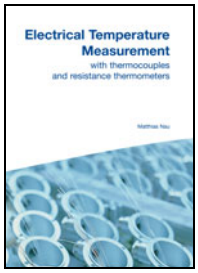
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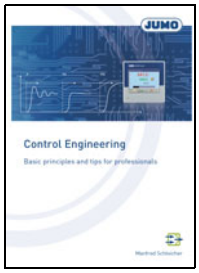
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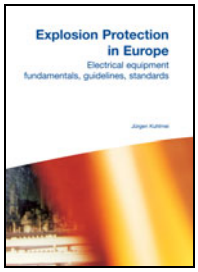
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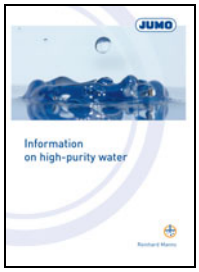
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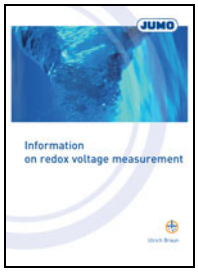
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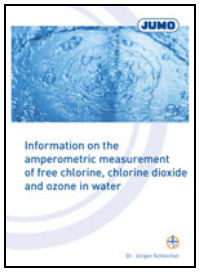
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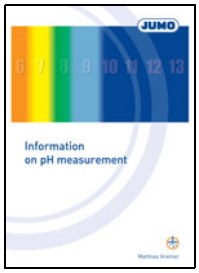
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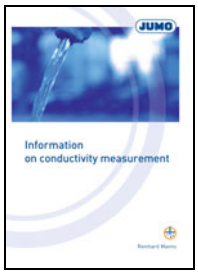
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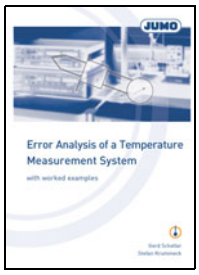
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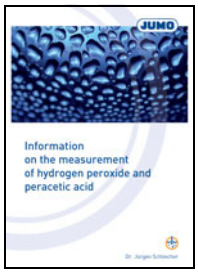
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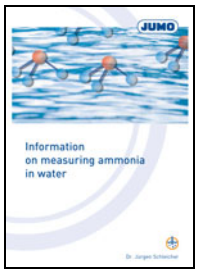
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