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Sensor for dissolved hydrogen with in-line calibration in aqueous media

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Hydrogen is becoming increasingly important as a process component in various areas of technology, often in relatively new applications. One example is in thermal power plants where the residual hydrogen concentration in boiler feedwater or water-steam-loop of power plants acts as an indicator of corrosion [1,2] or controlling the hydrogen concentration in the primary loop of a nuclear power plant [3,4]. Others include the removal of nitrate (NO^-_3) from drinking water [6] or catalytical removal of oxygen from water [5] where hydrogen concentration is used to monitor the progress of the catalytical reduction process (Fig.2). In the future, hydrogen measurement is also likely to become important in other wastewater treatment processes involving reduction [7].

The hydrogen in a water/steam loop of a power plant is mainly produced by the reaction between iron and water or steam. Thus the hydrogen concentration gives quantitative and qualitative evidence of the rate of

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corrosion and therefore corresponds to the buildup or destruction of the protective oxide layer inside pipes and boiler tubes. The hydrogen concentration ranges between a few µg/l (normal operation conditions) and several hundred µg/l during start-up (Fig.1).

In the primary loop of a nuclear power plant the hydrogen should eliminate the oxygen which is produced by radiolysis and reduce the electro-chemical potential (ECP) of the tube material.

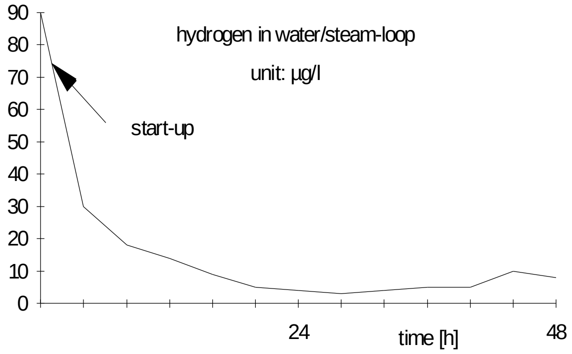

Fig.1

Hydrogen concentrations of around 20 mg/l occur in the denitrification of drinking water and the catalytic reduction of oxygen. These reactions take place on the surface of noble metal catalysts. In general it is important for the correct operation of the process to dose the exact amount of hydrogen.

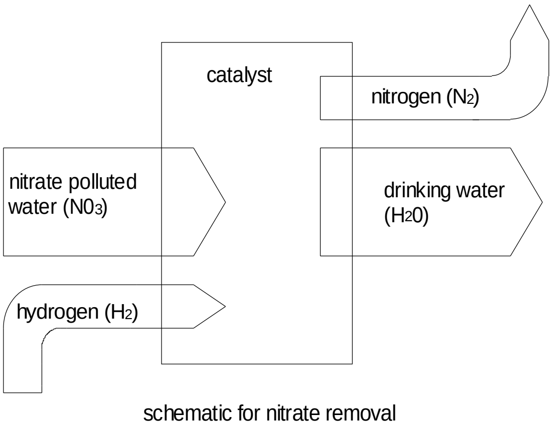

Fig. 2

Continuous quantitative measurement of dissolved hydrogen requires a specifically designed instrument. In particular, the design of such an instrument makes important demands on its reliability, ease of calibration and use, measuring range, maintenance and mechanical strength.

Calibration is especially important in the overall performance of the system. Ideally, the instrument should have in-line calibration, without the need for external calibration devices or changes in the plant's operating conditions. Simple, rapid calibration with automatic sensitivity correction allows the instrument to be calibrated more often, with consequent gains in performance and reliability.

1 Basic information and general description

This instrument functions in a potentiostatic mode with an open three-electrode system. The measuring electrode is made of solid titanium coated with platinum, the counter electrode is made of stainless steel and the reference electrode is silver/silverchlorid. The use of an open measuring electrode means that there are no membranes to block (Fig. 3).

For the measurement of dissolved molecular hydrogen (H_2) the fluid medium flows into the coaxial measurement cell between the platinum measuring electrode and counter electrode (Fig. 3). If the measuring electrode is at the correct potential, hydrogen is oxidized in the interphase boundary layer. The electrochemical reaction may be represented qualitatively as (1):[1)]

$$H_2 + 2 \cdot H_2O \Leftrightarrow 2 \cdot H_3O^+ + 2 \cdot e^- \qquad (1)$$

Equation (1) describes the anodic oxidation of hydrogen in acid media. The characteristic potential for this reaction - the potential at which hydrogen oxidation occurs in preference to other competing reactions - is measured by holding the potential of the measuring electrode steady with a potentiostat and comparing its value with that of the reference electrode. Under these conditions the rate of the electrochemical reaction is limited mainly by the rate of diffusion of hydrogen molecules to the electrode and the rate of diffusion of the reaction products H_3O^+ away from the electrode surface, so that the mass transport proceedings are dominated [8,9].

When the potential of the measuring electrode lies within the 'diffusion-limiting-current' area (Fig. 4), the electrochemical cell delivers an electric current whose size depends linearly on the concentration of dissolved hydrogen. The hydrogen molecule, which is transformed in H_3O^+, discharges at the counter electrode surface in the reverse electro-chemical reaction (1). This current, which is measured by the instrument's electronic processing unit, is known as the diffusion-limiting current, I_{diff}:

$$I_{\mathrm{diff}} = f(c_{\mathrm{H}_2}) \qquad (2)$$

This diffusion-limiting current mainly depends on the mass transport of the electrochemicaly active components, and hence on the hydrodynamics in the measuring cell. Therefore it changes significantly with the temperature and flowrate through the measuring cell. These relations can be described quantitatively by a defined cell geometry and state of flow condetions partially with methods of similarity theory [10]:

$$I_{\mathrm{diff}} = (1/\delta_{\mathrm{N}})(D_{\mathrm{ij}}\, A\, z\, F\, c_{\mathrm{H}_2}) \qquad (3)$$

The thickness of the Nernst-layer can be calculated approximately [11]:

$$\delta_{\mathrm{N}} \propto 3\, I_{\mathrm{diff}}^{1/2}\ \ W_0^{1/2}\ \ \nu^{1/6}\ \ D_{\mathrm{ij}}^{1/3} \qquad (4)$$

A second important influence on the measurement is the condition of the electrodes, in particular the

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[1)] An index is at the end of the article.

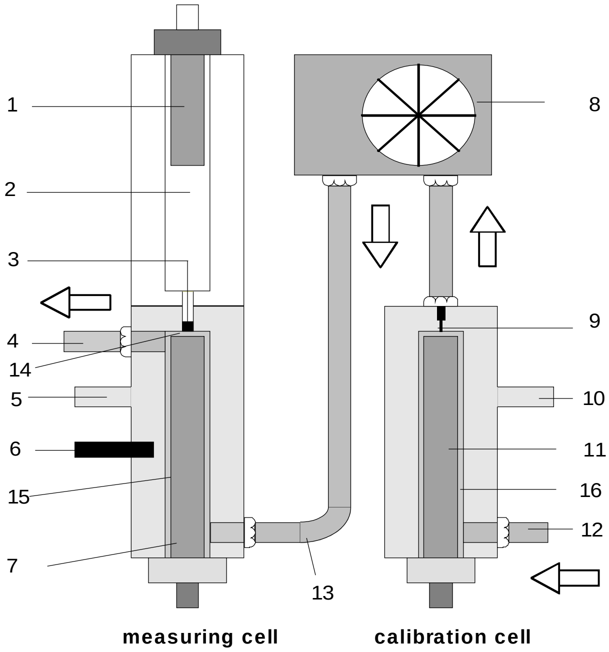
adsorptive and oxidative state of the electrode surface layer. This is independent of the flow conditions; instead it depends on the voltage between electrode and electrolyte and on the material of which the electrode is made, furthermore on sample matrix particularly either pH-value and the preliminary condition of the platinum sensor. These relations are manifold and are time dependent, so that they withdraw a general quantitative description with justifiable expense. On the other hand, a platinum metal as electrode material is without practical alternative, here a must. In practice the flowrate and temperature vary over wide ranges, but the instrument detects these parameters with built-in sensors.

But also the sample matrix can be fundamentally as well as currently be different. Those previous mentioned problems can be described by finding an empirical relation $I = f(D)$ and $I = f(T)$ from the experimental data. For applications this approximation will be described by a general mathematical function. With the help of calculation programs in the instrument's electronic processing unit the present electrical measured current become convert in the correct concentration value, for which also the notion compensation is common. Therefore, the topical measured electrical current is to be compensated on standard value.

2 The measuring system

Upstream of the measuring cell is the calibration cell (Fig. 3). This consists of two stainless steel electrodes, between which water (sample) is dissociated by a constant controlled current. According to Faraday's law, the rate of hydrogen production in the calibration cell is directly proportional to the electric current. The current can be exactly calculated by adding a defined difference of the hydrogen concentration Δc_{H_2} in the present sample flowrate to the preexisting current hydrogen level. This calibration current can be chosen depending on the applicable measuring range.

Figure 3
Schematics of the measuring system



1 Ag/AgCl reference electrode, 2 KCl-solution, 3 diaphragm, 4 sample outlet, 5 counter electrode, 6 temperature sensor, 7 platinum measuring electrode, 8 flowmeter, 9 diffusor, 10 calibration anode, 11 calibration cathode, 12 sample inlet, 13 tube line, 14 space of measuring reaction, 15 groove measuring cell, 16 groove calibration cell.

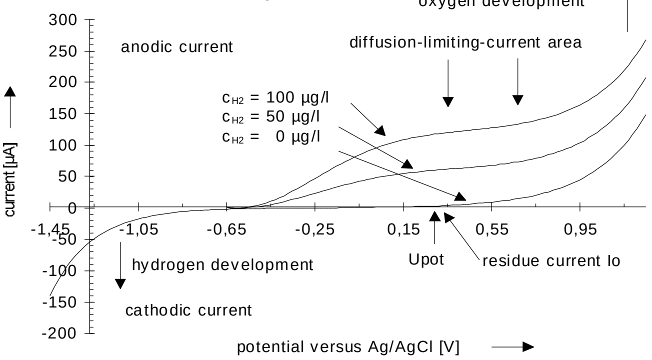
A constant electric current of 26,8 mA, for example, produces an increase in the hydrogen concentration of 100 µg/l at a flowrate of 10 l/h. This gives rise to a corresponding increase in the output current from the measuring cell, allowing the processing unit to calibrate the system automatically.

At the outlet of the calibration cell is a narrow diffusor tube which is mixing the fluid to ensure a uniform hydrogen concentration. After passing through the flowmeter the fluid flows into the measuring cell, passing through the annulus between the platinum measuring electrode and counter electrode. The dimension of the annulus has been optimized to give repeatable, laminar flow between the electrodes.

3 Results and discussion

Using laboratory equipments a typical potential-current diagram of the anodic hydrogen reaction at galvanic coated measuring electrodes is noted (Fig. 4). The following experiments were carried out in co-operation with the Technische Fachhochschule Berlin (TFH).

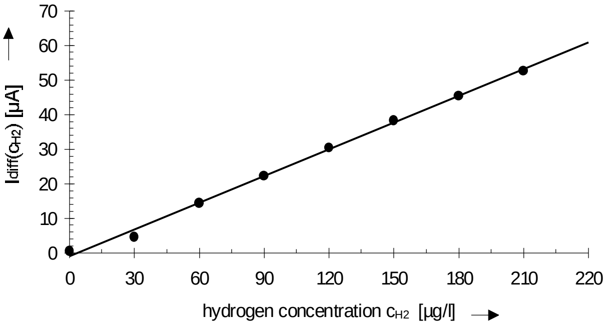
Figure 4
Potential-current-diagram



For practical analyses the entire range of voltage in the diffusion-limiting current area is not generally available. Instead, a specific voltage value is chosen based on the electrode design and, preferably, the pH range in which the instrument will operate. Furthermore, it must carry out an optimization of the „zero-indication“ if no hydrogen is present in the sample. Especially it must lead to an optimization of the catalytic behavior of the platinum electrode surface and reproducibility during drastic change of hydrogen concentration, for example, in case of low hydrogen concentration during starting and finishing the calibration procedure. In this case the platinum electrode shows more or less a hysteresis which can be reduced by optimization of the measuring potential.

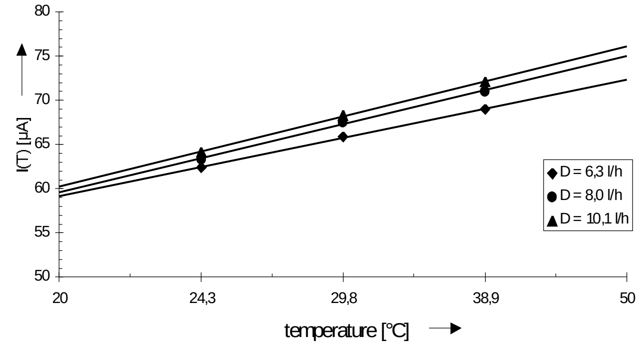
In Fig. 5 a typical calibration curve of a diffusion-limiting current as a function of hydrogen concentration is shown. It is approximately a straight line, showing how effectively the instrument can be when operating at an optimized voltage for the measuring electrode.

Figure 5
Relation between hydrogen concentration and diffusion-limiting-current



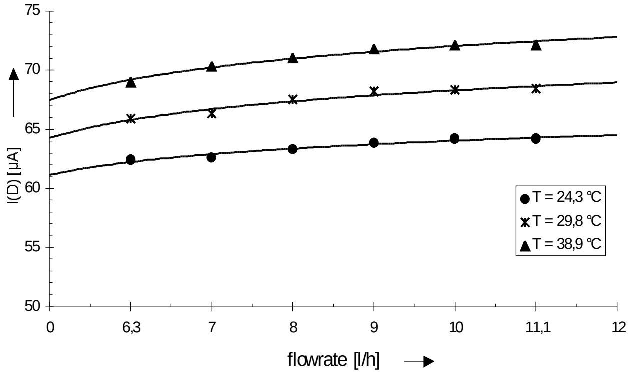
Parameter: c = 150 µg/l, pH value 9,1, Upot = 250 mV

Figure 6
Relation between current and temperature



Parameter: c = 150 µg/l, pH value 9,1, Upot = 250 mV

Figure 7
Relation between current and flowrate

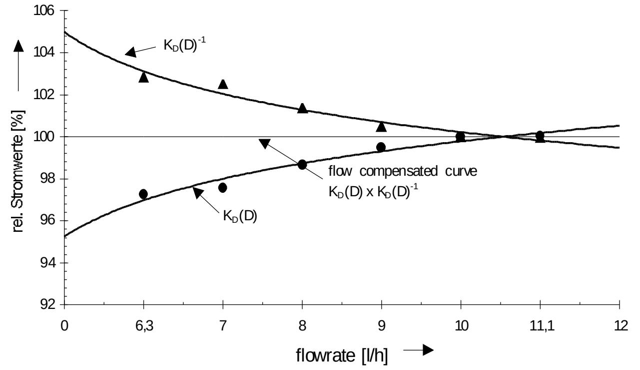


Parameter: c = 150 µg/l, pH value 9,1, Upot = 250 mV

The practical dependences of the state of coverage of the electrode as well as on the flowrate and temperature have been experimentally determined and have as a result been mathematically approximated. Diagrams Fig. 6 and Fig 7 show these relationships.

The developed compensation procedure works with three compensation factors which have been determined by the measured data: $k_T(T)$ for the temperature dependence, $k_D(D)$ for the flow dependence as well as $k_I(T,\Theta)$ for the state of the surface of the electrode. The factors $k_T(T)$, $k_D(D)$ and $k_I(T,\Theta)$ are coefficients of the approximation equation.

Figure 8
Diagram of the relative current values



Essentially $k_I(T,\Theta)$ determined by the calibration procedure. The compensation procedure is based on standard or referenced values for temperature of 20 °C and flowrate of 10 l/h. One transforms the present current values like they would be measured in a system under standard conditions. Any change of the actual parameters temperature and flowrate are recorded by the microprocessor unit in the electronic part. An appropriate measuring equation may have the following form:

$$c_{H_2} = I(T,D,\Theta)\, k_I(T,\Theta)\, k_T(T)^{-1}\, k_D(D)^{-1} \qquad (5)$$

One get the relative functions $k_T(T)$ and $k_D(D)$ from the determined data $I = f(D)$ and $I = f(T)$ as well as $I = f(T,D,\Theta)$ by dividing them by the respective standard current values at relative values for temperature of 20 °C and flowrate of 10 l/h. If a measuring current at an arbitrary temperature value and flowrate value will be multiplied by the inverse relative functions $k_T(T)^{-1}$ and $k_D(D)^{-1}$, one always get the values under standard conditions, like in Fig. 8, where as an example the flow dependence is shown.

Since $k_I(T,\Theta)$ has been determined during at the calibration procedure one receives ultimately calculated data, which is a good approximation independent of the different influences and indicates the actual value of the dissolved hydrogen concentration exactly.

The instrument has been tested in practice at a Berlin power station. High-pressure steam passed through a cooler and pressure reducing valve before being fed to the analyzer's measuring cell. After calibration, the device indicated a hydrogen concentration of 0,5 µg/l. This is the usual value for this plant, which is known from other analyses.

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Notation

A	[cm^2]	area of reaction
c_{H_2}	[µg/l]	molecular hydrogen bulk concentration
D	[l/h]	flowrate

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D_{ij}	[cm^2/s]	diffusion coefficient of the electrochemical active component
F	[As/val]	Faraday-constant
I_{diff}	[µA]	measuring current, diffusion limiting current
$k_D(D)$	[-]	compensation coefficient flow
$k_T(T)$	[-]	compensation coefficient temperature
$k_I(T,\Theta)$	[-]	calibration constant, at the same time compensation coefficient surface state of the electrode
T	[°C]	temperature
U_{pot}	[V]	optimized measuring electrode potential versus Ag/AgCl
W_0	[cm/s]	characteristic velocity in the groove
z	[-]	charge number
δ_N	[cm]	thickness of the Nernst-layer
Θ	[-]	adsorptive and oxidative state of the platinum electrode
ν	[m^2/s]	kinematic viscosity

Reference

[1] KITTEL, H., SCHLIZIO, H.
VGB KRAFTWERKSTECHNIK 56 (1976), H. 1 S. 33-45

[2] SCHLIZIO, H., u. a.,
VGB KRAFTWERKSTECHNIK 65 (1985), H. 7 S. 687-693

[3] FEJES, P.
VGB KRAFTWERKSTECHNIK 66 (1986), H. 12 S. 1162-1177

[4] COWAN, R. L.
VGB KRAFTWERKSTECHNIK 75 (1995), H. 8 S. 739-744

[5] THOMAS, P.
VGB KRAFTWERKSTECHNIK 61 (1981), H. 1 S. 59-61

[6] VORLOP, K. D., TACKE, T.
Chem.-Ing.-Tech. 61 (1989) H. 10 S. 836-837

[7] MAIERER, M., u. a.
VGB KRAFTWERKSTECHNIK 75 (1995), H. 10 S. 902-907

[8] HAMAN, C. H., VIELSTICH, W.
Elektrochem. II, Weinheim 1981

[9] VETTER, J. K.
Elektrochemische Kinetik, Springer, Berlin 1961

[10] LEVICH, V. G.
Physiochemical Hydrodynamic, Prentice Hall, New York 1962

[11] VIELSTICH, W.
Z. Elektochem. 57 (1953) S. 646