doi:10.2533/chimia.2009.643 Chimia 63 (2009) 643–646 © Schweizerische Chemische Gesellschaft

Metrology in Chemistry for pH and Electrolytic Conductivity Traceability Dissemination

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Abstract: pH and electrolytic conductivity are important metrological quantities for several areas of industry. To get reliable results it is necessary to calibrate measuring instruments and devices regularly. For this purpose certified reference solutions are needed. DKD-K-06901 is a manufacturer of certified reference solutions and offers calibration services in the field of analytical chemistry. There are three accredited calibration procedures for the determination of pH used by ZKM - ANALYTIK - GmbH. A new calibration procedure for electrolytic conductivity was established by experts in DKD-K-06901 as the result of a development project in cooperation with National Metrology Institutes. The validation of all procedures is guaranteed by the participation in national and international comparison measurements. Furthermore DKD-K-06901 is actively involved in the work of technical and standardisation committees for developments of analytical quantities.

Keywords: Accreditation · Calibration · Electrolytic conductivity · pH · Reference solutions

1. Introduction

The determination of pH and electrolytic conductivity is essential to ensure the quality standards of pharmaceutical products, health care, water analysis, biochemistry and in the chemical industry.

In this context, the issue of continuous quality and process control is significant. To fulfil this point sophisticated measuring systems are an important element. Metrological traceability of the measurement results is essential in order to fulfil the legal requirements to ensure the required measurement correctness with consideration to the expanded measurement uncertainty.

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2. Metrological Hierarchy and Measurement Principles

Certified reference solutions for electrolytic conductivity and pH are the metrological basis for industrial purposes within the traceability hierarchy. There is a decades-long experience on the field of analytical quantities in the DKD-K-06901, especially in the manufacturing of reference materials and solutions.

In the frame of the German calibration service 'Deutscher Kalibrierdienst (DKD)' standard procedures are approved as a precondition for the calibration of measuring instruments, and measurement systems. As an accredited calibration laboratory DKD-K-06901 is therefore able to determine reference values of reference solutions traceable to the SI. pH is defined by a conventional method which was published again by IUPAC in 2002.[1] For pH the traceability to the SI is not possible to suffiently low uncertainty.

The pH is defined as negative decimal logarithm of hydrogen-ion activity a_H:

$$pH = -\lg\left(\frac{a_H}{m^\circ}\right) = -\lg\left(\frac{m(H^+)\cdot\gamma(H^+)}{m^\circ}\right) \qquad (1)$$

where m° is the standard molality (1 mol·kg^{-1}).

The hydrogen-ion activity on the molality scale is the product of molality of the hydrogen ion $m(H^+)$ and the corresponding activity coefficient $\gamma(H^+)$. The activity coefficient of ions cannot be measured for a single ion type alone but only a mean activity coefficient is measurable. That is the reason why the pH cannot be measured directly according to its definition.

The standard hydrogen electrode realised by a Harned cell is agreed internationally to serve as the device for the measurement of the pH at the highest metrological level.

The reference values of the pH standards are determined traceable to internationally agreed certified references.[2]

The metrological traceability hierarchy for the measuring quantities pH and electrolytic conductivity is shown in Fig. 1 and Fig. 2.

Fig. 1 shows the unbroken chain from the National Metrological Institutes (NMIs) over accredited DKD laboratories directly to the application level.

There are three calibration procedures for pH, accredited by the DKD accreditation body according to ISO/IEC 17025:2005:[3]

i) Absolute measuring method: standard hydrogen electrode device using Harned cells
ii) Comparison method: differential potentiometry
iii) Secondary procedure: multi-point calibration (five measuring points) with a glass electrode system

With the standard hydrogen device (Harned cells) it is always possible to measure pH and verify the pH of primary standard buffer solutions.[1]

Analogically Fig. 2 shows the unbroken chain from the National Metrological Institutes over accredited DKD laboratories directly to the application level.

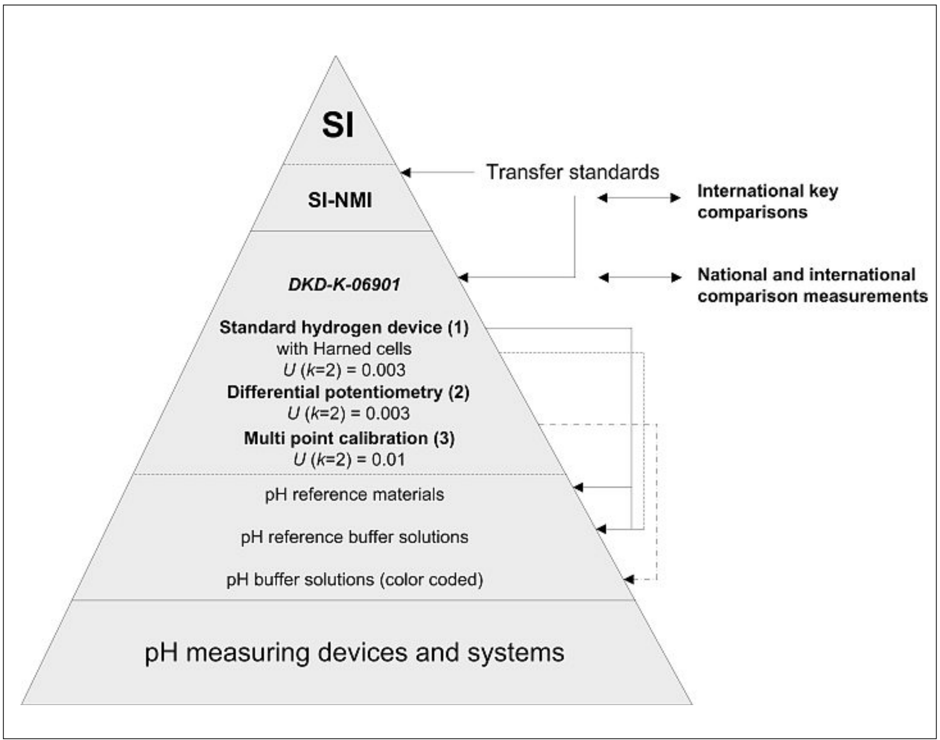

Fig. 1. Metrological hierarchy for pH.

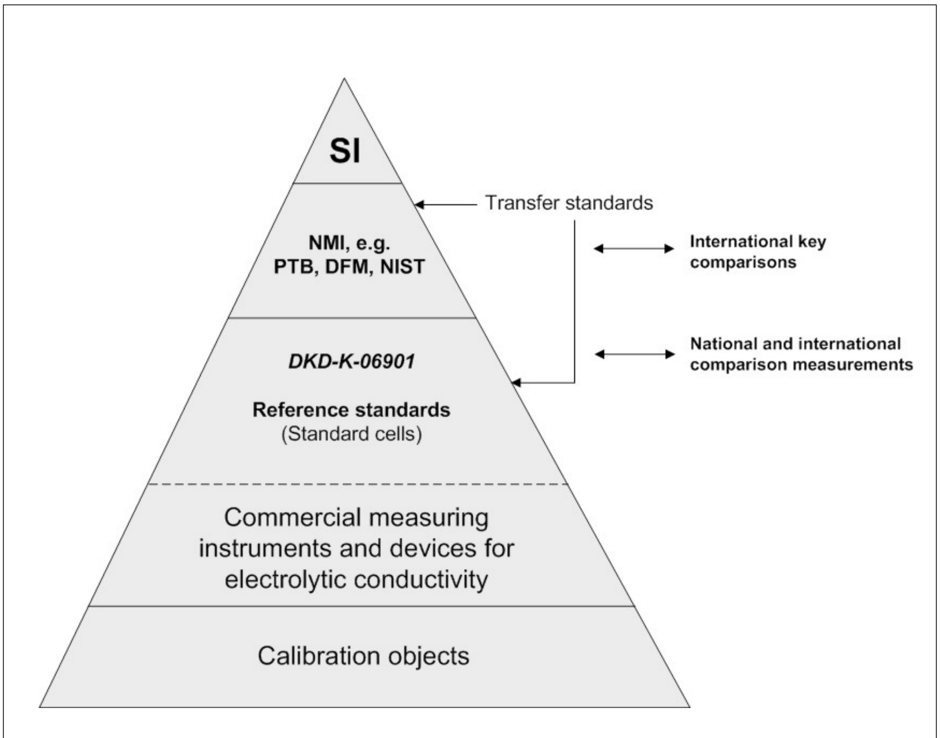

Fig. 2. Metrological hierarchy for electrolytic conductivity.

To ensure the metrological traceability, it is essential for an accredited calibration laboratory to take part in comparison measurements. DKD-K-06901 takes part continuously in national and international comparisons. Often the sample used in international comparisons among NMIs, so-called key comparisons, is the same as used for comparisons at the level of calibration laboratories. The results of the key comparison are accessible at the BIPM database and for the DKD comparisons at the DKD homepage.[4,5] Thus a strong link exists between the calibration laboratory and the national metrology institutes. With this close relationship to the national NMI, the PTB, the calibration laboratory DKD-K-06901 is able to offer its customers reference values with sufficiently small combined measurement uncertainties needed for industrial level as well as for high precision measurements carried out in research institutes and universities.

But there is the principle, not as precise as possible but as precise as is necessary to measure.

This means not to supply results with lowest possible expanded uncertainty but results with uncertainties that are required for the task of the user, 'fit for purpose'.

DKD-K-06901 offers *customer specific, 'tailored' reference solutions* with respect to the measuring range, the target uncertainty and the amount of sample needed.

Fig. 3 shows frequently used coloured industrial buffer solutions with lower requirements to measurement uncertainties. The manufacturing of industrial buffer solutions shall be applied according to international standards, *e.g.* DIN 19267.[6,7]

Of course the traceability to national standards is also mandatory for industrial buffer solutions.

3. Research and Development

3.1 *Conductivity*

Research and development work for new calibration procedures is a vital pillar in the strategy of an accredited calibration laboratory. In cooperation with the specialists from PTB (Germany) and DFM (Denmark) it was possible to develop a new calibration procedure for electrolytic conductivity κ using standard cells.[8–11] Their basic approach is to divide the range of electrolytic conductivity κ from 1.3 $\mu S\cdot cm^{-1}$ to 150 $mS\cdot cm^{-1}$ into sub-ranges (Fig. 4). For each range a standard cell was built. The cells differ in the distance between the electrodes and therefore in the cell constant K (Eqn. 2).

$$\kappa = \frac{1}{R} \cdot K \qquad (2)$$

In this way it is possible to optimise the measurement conditions for each calibration solutions and to decrease the measurement uncertainty.

The determination of the conductivity κ requires the knowledge of the resistance R of the solution, which is mainly dependent on the ions involved (types of ions in solution, charge of ions, mobility of ions, temperature of electrolyte, *etc.*). The cell constant K itself is strongly influenced by geometrical factors (electrode distance, active electrode surface). It is determined using known calibration solutions with traceable conductivity

Fig. 3. Colour-coded pH-buffer solutions manufactured by DKD-K-06901.

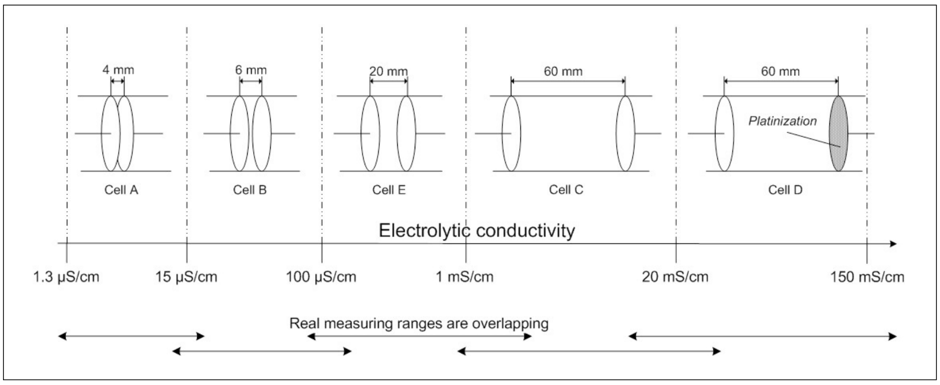

Fig. 4. Operating ranges of standard measuring cells.

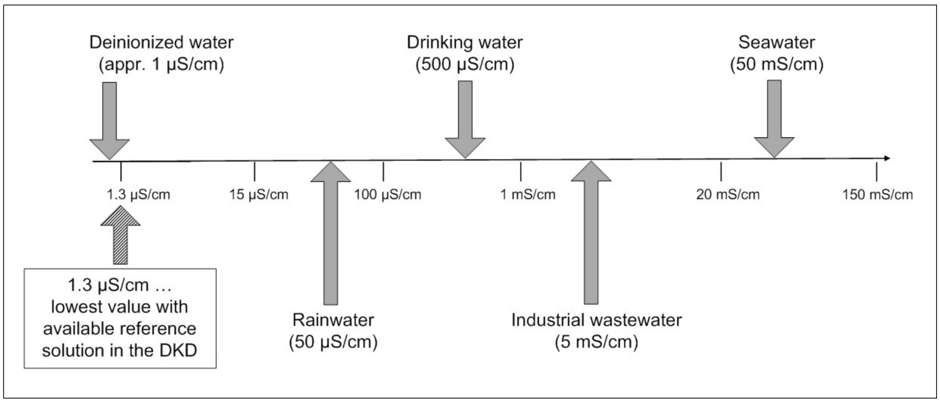

Fig. 5. Examples of different waters and their electrolytic conductivity.

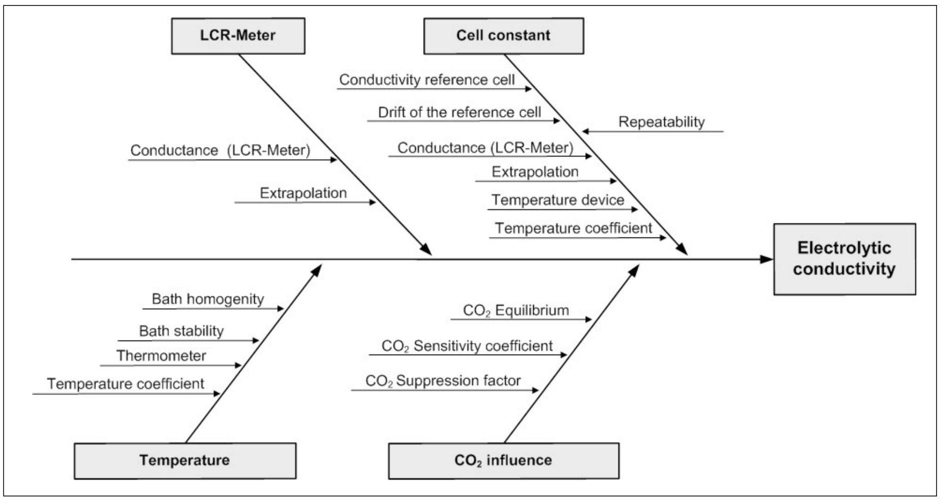

Fig. 6. Cause and effect diagram for measurement uncertainty during determination of electrolytic conductivity using standard cells.

standards. The solution resistance R is evaluated from the real part Re(Z) of the measured complex impedance Z using a linear regression by extrapolation to high frequencies f:

$$R = \lim_{1/f \to 0} \left[\mathrm{Re}\{Z(f)\} \right] \tag{3}$$

The background of the subdivision of the measurement range for electrolytic conductivity was the different needs of customers. Different areas of industry and research use waters with different electrolytic conductivity (Fig. 5).

The results of the development project were presented in 2007 at the NCSLI Conference in Saint Paul (USA) and were published.[12]

There is not only an influence from the cell constant on the results and the measurement uncertainty. A number of factors had to be taken into consideration during the development process (Fig. 6).[13] There are other factors which influence the measuring process, *e.g.* the LCR meter used and the temperature.[14–16] For lower electrolytic conductivities the influences of carbon dioxide in air becomes more and more important (Fig. 6).[8–10]

With this metrological principle also solutions from the Hamilton Bonaduz AG were measured at DKD-K-06901 and additional at the National Metrological Institute DFM. The measuring results showed a good agreement.

3.2 *Training and Knowledge Dissemination*

Their long-term experience in the measurement of analytical quantities like pH and electrolytic conductivity and in legal matters of quality assurance enables specialists of DKD-K-06901 to disseminate their knowledge in training courses and consultations for industrial partners.[17] The participants of the training activities are newcomers and also experienced specialists in the field of metrology from various countries. They are trained on all important topics for accredited calibration laboratories such as measuring principles, technical details, measurement uncertainties according to GUM, quality trail documents and the requirements of ISO/IEC 17025.[1,18,19]

Reference solutions for electrolytic conductivity and pH reference buffer solutions are manufactured, stored and monitored regarding shelf life and stability according to the regulations of a quality management of ISO 9001:2008 (IQNet registration number: 054774 QM) and ISO/IEC 17025:2005.[3,19] The processes are constantly monitored and supervised by specialists.

3.3 *Extension of pH Calibration Scale*

In line with the requirements of the industry DKD-K-06901 works together with the PTB on a project to investigate the temperature behaviour of pH reference buffer solutions up to 80 °C. The aim is to provide pH-reference buffer solutions over a wider temperature range as required for instance by the pharmaceutical and biotechnology industry. DKD-K-06901 also substantial contributes to the work of the pH standard committee within the DKD as a member.

4. Conclusions

Based on the long-term experience and the international recognized research DKD-K-06901 with the products – reference solutions and calibration services – is a reliable partner for the users in the industry, at universities and at research institutions.

Acknowledgements

The authors would like to acknowledge Petra Spitzer (PTB) and Hans D. Jensen (DFM) for the possibilities to take part in international key comparison measurements as a participant in the background.

Received: June 25, 2009

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