

Metrological Traceability Concept for Electrolytic Conductivity and pH

Steffen Seitz^{*a}, Petra Spitzer^a, Pia T. Jakobsen^b, and Hans D. Jensen^b

Abstract: The metrological traceability concept links measurement results by a chain of calibrations to the quantity values of primary standards, which are realised by primary measurement procedures. These procedures undergo periodical international comparison measurements, in order to guarantee worldwide comparability of measurement results. In this article we demonstrate how the metrological traceability concept applies to electrolytic conductivity and pH measurements. Furthermore we will outline promising activities in current metrological research to extend traceability of electrolytic conductivity measurements down to the low $\mu\text{S cm}^{-1}$ level.

Keywords: Electrolytic conductivity · Metrological traceability · pH · Primary measurement procedure

1. Introduction

Electrolytic conductivity and pH are among the most frequently measured analytical quantities, since these measurements are low cost, easy to perform and lead to rapid results. These quantities are determined in environmental monitoring and clinical chemistry as well as in food production, pharmacy, industrial processes, power plants and many other applications. They serve as important parameters for process control and quality assurance. Therefore, metrological traceability of the measuring results is crucial in order to guarantee their reliability.

In general, a measurement result consists of a quantity value, which is indicated by a measuring system, and its measurement uncertainty.^[1,2] Whenever it is subject to legal regulations, it must be indicated in generally valid and consistent units. The same holds for measurement results, which must be compared to each other, even if they are measured by different people, with different equipment, at different times and places. This is the idea behind metrological comparability of

measurement results. Nowadays, to meet this requirement a measurement result has to be linked to a unit in the *Système International d'Unités* (SI).^[3,4] In case this is not possible, it must be linked to internationally agreed and stated references. For many measured physical-chemical quantities, this link is established by a hierarchy of calibration measurements. That is the measurement result of a (routinely performed) calibration is compared (and adjusted) to the quantitative value provided by a measurement standard like a reference material for instance. The quantitative value of the measurement standard (and its uncertainty) is assigned, using a measuring procedure that has to be calibrated likewise and so on. This so-called traceability chain leads to a primary standard, whose quantity value is realised by a primary measurement procedure. Traceability to the SI is given if the quantity value of a primary standard can be quantitatively related to the basic measurands of the procedure. Additionally, the corresponding measurement results have in turn to be traceable likewise to the technical realisations of the basic SI units. Since every uncertainty calculation has also to account for the uncertainty of the measurement standard, obviously a primary standard shows the lowest uncertainty, whereas the measurement uncertainty increases with every calibration level. The Fig. illustrates a simple traceability chain for electrolytic conductivity. Primary measurement procedures are typically realised by National Metrology Institutes (NMIs). These conduct international comparison measurements under the umbrella of the International Bureau of Weights and Measures (BIMP), in order to establish the comparability of national measurement standards.^[5] Electrolytic conductivity and pH comparisons are organised by the Consultative Committee on Metrology

in Chemistry (CCQM) Electrochemical Analysis Working Group (EAWG).^[6]

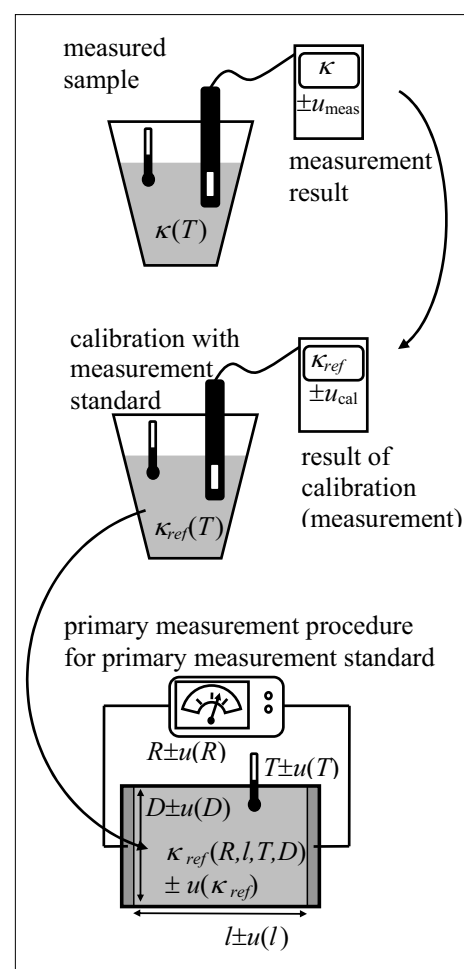


Fig. Simple metrological traceability chain to the SI for the result of an electrolytic conductivity measurement. It illustrates the link between the quantitative conductivity value κ , indicated by the measuring device, and the SI quantities resistance (R), length (l , D) and temperature (T). Note that every measurement result consists of a quantity value y and its uncertainty $u(y)$.

*Correspondence: Dr. S. Seitz^a

Tel.: +49 531 592 3019

Fax: +49 531 592 3015

E-mail: steffen.seitz@ptb.de

^aPhysikalisch-Technische Bundesanstalt (PTB)

Bundesallee 100

D-38116 Braunschweig, Germany

^bDanish Fundamental Metrology DFM

Matematiktorvet 307

DK-2800 Kgs. Lyngby, Denmark

2. Principles of Primary Electrolytic Conductivity Measurements

Primary measurement procedures to realise primary standards for electrolytic conductivity are based on resistance, length and temperature measurements. A good overview about various methods is given in ref. [7]. In principle, the electrolytic conductivity κ_{ref} of a primary reference solution at a defined temperature T can be calculated from Eqn. (1).

$$\kappa_{ref} = \frac{K}{R} \quad (1)$$

with R being the resistance of the solution in a measuring cell and K being the so-called cell constant. Under the condition of a specific cell design the cell constant can be determined by geometric measurements, while the bulk resistance of the solution can be deduced from measured impedance spectra.^[8] Since all these measurement results are traceable to the SI, this method allows the realisation of primary conductivity standards whose conductivity values are traceable to the SI. Some NMIs prepare conductivity reference solutions, by following a strict preparation recipe. In this approach the conductivity value stated in the corresponding preparation instruction is assigned to the solution.^[9] Since this conductivity value is not the result of a primary measurement procedure of the *actually* prepared solution, the traceability chain (to the SI) is broken at that stage. Thus, measurement results traced back to such reference solutions are strictly speaking not traced back to the SI, even if the stated values have once been measured traceable to the SI.^[10,11] However, up to now electrolytic conductivity comparison measurements among the NMIs have shown both methods to lead to consistent conductivity measurement results within the stated measurement uncertainties. The second approach therefore is still accepted practice.

3. Extending the Measuring Range of Primary Conductivity Measurements

The current conductivity measuring range, in which primary conductivity standards are ensured by international comparison measurements, ranges from 50 $\mu\text{S cm}^{-1}$ up to 5 S m^{-1} .^[12,13] Present activities in metrological research aim to extend this region at the low end down to the low $\mu\text{S cm}^{-1}$ range, where aqueous reference solution are unstable due to the influence of atmospheric carbon dioxide.^[13]

Carbon dioxide dissolves in water and partly forms carbonic acid. By that it contributes to the measured conductivity value in the order of 1 $\mu\text{S cm}^{-1}$, depending on the partial CO_2 pressure present during the measurement. Thus, as soon as it is exposed to the atmosphere, the actual conductivity of an aqueous reference solution changes significantly with respect to its calibrated value. This consequently increases the uncertainty of a conductivity measurement traced back to aqueous reference solutions. A possibility to overcome this problem is to use solvents of high viscosity. First because they reduce the solubility of atmospheric CO_2 . Secondly, since ion mobility is decreased, they allow for higher electrolyte concentrations at low conductivity values, which minimises the relative conductivity contribution of remaining (hydro) carbonate ions.

A first comparison study of primary conductivity measurements of a commercial 5 $\mu\text{S cm}^{-1}$ glycerol solution resulted in a significant difference of more than 1 % between the conductivity values determined by the Danish and the German NMIs, the Danish Fundamental Metrology (DFM) and the Physikalisch-Technische Bundesanstalt (PTB). Presumably the common procedures to determine the resistance of the solution cannot be adopted for low conductive and viscous solutions without further investigation.^[7,14,15] The deduction of the resistance is performed on the basis of an equivalent circuit, which models the impedance of the cell-solution system. But data modelling and resistance deduction often are not specified. A follow-up study therefore included, in addition to more participants, more detailed requirements to measurements and reporting. In particular a careful analysis of the impedance spectra over an extended frequency range was demanded. At present the study is ongoing, but a first evaluation indicates that the difference between DFM and PTB can be reduced below 0.1%. So traceable measurements in the low conductivity region seem to be possible within an acceptable measurement uncertainty.

In the near future the conductivity range for traceable measurements will be further extended down to the level of ultra pure water of about 55 nS cm^{-1} . This issue is currently one of the subjects of an European metrology research project (EMRP-TP2 JRP10), in which the NMIs of Germany, Denmark, Italy and Sweden cooperate.

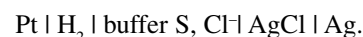
4. Primary Measurement Procedure for pH

The pH as a measure of the acidity of a solution is defined as the negative decadic

logarithm of the activity of the solvated hydrogen ion.^[16]

$$\text{pH} = -\lg a_{\text{H}} = -\lg(m_{\text{H}} \cdot \gamma_{\text{H}} / m^{\circ}) \quad (2)$$

where a_{H} is the relative (molality basis) activity, γ_{H} the molal activity coefficient of the hydrogen ion H^+ at the molality m_{H} , and m° is a standard state chosen to be equal to 1 mol kg^{-1} of hydrogen ions. The definition involves a single ion activity and cannot be realised without non-thermodynamic assumptions being made. In 2002 the International Union of Pure and Applied Chemistry (IUPAC) issued a recommendation for a primary measurement procedure for pH.^[17] It is based on the measurement of the potential difference of a potentiometric cell without liquid junction, involving a selected buffer solution, a platinum hydrogen gas electrode and a silver/silver chloride reference electrode, often called Harned cell.^[18]



The primary buffer solutions recommended by IUPAC today establish the so-called multipoint pH protocol, developed by Bates and co-workers at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST).^[19] Each primary buffer is a dilute aqueous solution at ionic strength equal or smaller than 0.1 mol kg^{-1} . NMIs use this primary method for pH to measure the pH of primary reference buffer solutions at the top of the traceability chain.

Traceability of the pH value measured to the SI can be established for the pH values of these buffer solutions if the expanded uncertainty attributable to the non-thermodynamic assumption, the Bates-Guggenheim convention, is taken into account.^[20] Unfortunately, the measurement uncertainty contribution arising from the use of this convention is 0.01 (expanded measurement uncertainty, $k = 2$, corresponding to a level of confidence of approximately 95%). The experimental expanded measurement uncertainty ($k = 2$) obtained for a pH value of a typical primary buffer solution is, however, only 0.004. Values of pH that include all sources of uncertainty *except* that of the Bates-Guggenheim convention, as is the common practice at most of the NMIs, are considered conventional pH values, which are sufficient for most applications.

In 2007 approximately 20 NMIs performed primary pH measurements and participated in international so called key comparisons (KC), organised by CCQM. Five KCs for pH have been organised

until the end of 2008.^[12] The agreement between the results and the key comparison reference value (KCRV) expressed as a standard deviation is about 0.003 for experienced laboratories and about 0.007 for all laboratories, including newcomers. Participating NMIs in the pH KCs have observed a number of instrumental and methodological problems. Pilot Studies present an opportunity to investigate issues, such as the stabilisation time of Ag/AgCl electrodes, that have caused problems in KCs. Pilot Studies are also used by newcomers to test their measurement capabilities.^[21]

Operating the Harned cell at the highest metrological level is possible for NMIs but would not be suitable for calibration and reference laboratories and for routine measurements, respectively. There are a number of cells having liquid junctions, which may be used for the determination of the pH of a secondary reference buffer solutions by comparison with a primary buffer solution.^[22,23] A metrological traceability chain of a routine laboratory measured quantity value of pH is depicted in ref. [24].

The Bates-Guggenheim convention is only valid at ionic strengths up to $0.1 \text{ mol} \cdot \text{kg}^{-1}$. For applications in clinical chemistry and in environmental samples (e.g. rainwater, seawater), pH reference buffer solutions with ionic strengths more similar to these samples are expected to improve the comparability of measurement results in these matrices. Further investigations into solution theory and into the concept of single-ion activity are necessary to overcome the present limitations

for the primary procedure for pH measurement. One approach is the Pitzer model of electrolytes which uses a virial equation approach to provide an improvement in the primary method.^[25]

Progress in disseminating the traceability to the user in the field is expected as an outcome of a new IUPAC project: 'Comparable pH measurements by metrological traceability for improving the scientific basis and broadening the applicability of pH measurement'.^[26]

5. Conclusion

Electrolytic conductivity and pH are measured in manifold applications. Although they are rather established measurands, there is an ongoing need for metrological research in primary measurement procedures in order to guarantee metrological traceability of measurement results in new measuring ranges and new fields of applications.

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