

Improvement in the reliability and comparability of pH measurements

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Abstract

To meet the requirements for quality control and other technical specifications a corresponding need exists for traceability in pH measurement results.

The prerequisite for the international acceptance of analytical data is reliability. To measure means to compare. Comparability entails recognised references to which the standard solutions used for the calibration of pH meters can be traced back.

For analytical data to be internationally accepted, it is necessary to demonstrate the equivalence of the national traceability structures, including the national measurement standards. A report on the results of key comparisons and other international initiatives to improve the consistency of the results of measurement for both quantities is given.

1. Introduction

pH is among the most frequently measured physical-chemical parameters in many areas of application, e.g. health care and safety, biochemistry and environmental monitoring are being among the most important ones. Statements of the measurement uncertainty based on traceability to international recognised references are required by regulatory bodies or by the international quality assurance standard ISO EN 17025 [1] in general.

Moreover recent research in environmental science and in biochemistry has given evidence that the measurement uncertainty in pH forms a central contribution to the uncertainty budget of thermodynamic data as well as of geochemical transport models [2].

Confidence in the reliability of analytical data requires the complete knowledge of the chain of traceability linking the measured value of the quantity in the sample to a unit in the International System of Units (SI) or, where that is not possible, up to international agreed and stated references [3].

For the pH, over the last decade, work has been carried out in a number of countries to build a metrologically based measurement infrastructure within a national framework. The traceability chains for pH will be described in the following paragraphs.

2. The quantity pH

More than a hundred years ago, in 1909, Soerensen [4] defined pH in terms of the concentration with a scale of 0–14 (at 25°C) derived from the ionic product of water ($K_w = 10^{-14} \text{ mol} \cdot \text{L}^{-1}$). Some years later, the concept of activity was introduced by Lewis, and in 1923 Debye and Hueckel published their theory for strong electrolyte solutions. On the basis of this knowledge, Soerensen and Linderstroem-Lang [5] suggested a new pH definition in terms of the activity of hydrogen ions in solution:

$$\text{pH} = -\lg a_{\text{H}} / m^0 = -\lg(m_{\text{H}}\gamma_{\text{H}} / m^0) \quad (1)$$

where a_{H} is the activity and γ_{H} the molal activity coefficient of the hydrogen ion H^+ at the molality m_{H} , and m^0 is the standard molality: 1 mol kg^{-1} .

Definition (1) involves the single ion activity coefficient of the hydrogen ion taken into account the ionic interactions in the solution. Activity coefficients of individual ions cannot be measured without non-thermodynamic assumptions being made. Therefore a special feature of pH is that traceability does not extend to the SI at the uncertainty level necessary for practical pH measurements. International recognised primary pH standards related as closely as possible to the thermodynamic definition of pH and provisions for sample pH to be traceable to the primary references are needed.

3. The traceability chain

The IUPAC (International Union on Pure and Applied Chemistry) recommendation [6] has formed the basis for the standardisation of pH measurements since 1985. The IUPAC recommended two different approaches for assignment of values to pH standard buffer solutions. Their use yields to different pH values for the same buffer solution [7] and was not sufficient to establish confidence in the measurement results.

The need for mutual acceptance of analytical data on the basis of demonstrated traceability and the confusion resulting from the ambiguous IUPAC recommendation led the IUPAC Analytical Chemistry Division (V) and the Division on Physical and Biophysical Chemistry (I) to form a Working Party on pH to develop a new pH concept. The measurement procedures described in the recently published provisional recommendation [8] are applied by national metrology institutes (NMIs) and by accredited calibration laboratories to determine pH values of a restricted number of primary and secondary pH reference materials with stated uncertainty. Because the pH standards must maintain their pH values even when contaminated with small amounts of acids or bases they are buffer solutions.

3.1. The primary measurement procedure

The pH measurement is carried out by measuring the potential difference of the electrochemical Cell I containing a selected buffer, the hydrogen ion sensing platinum hydrogen electrode and the silver/silver chloride reference electrode, often called Harned cell.

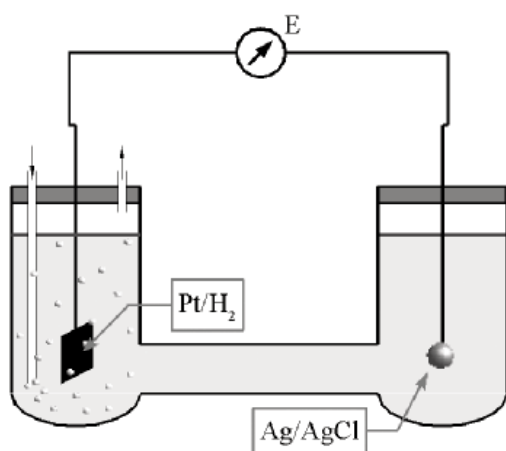


Figure 1. Schematic design of a Harned cell.

As a liquid junction potential is avoided, the cell potential consists merely of the electrode potentials. Chloride ions are added to the chloride free buffer at several chloride molalities in order to stabilize the potential of the silver-silver chloride electrode. The measurement procedure involves an extrapolation of the measured potential difference to zero chloride molality.

The primary method for pH now also recommended by the IUPAC based on the Bates-Guggenheim convention [9]. Bates and Guggenheim for low ionic strength $I \leq 0.1 \text{ mol kg}^{-1}$ suggested an approximation for the single ion activity coefficient on the basis of the Debye-Hückel theory of strong electrolytes.

The convention assumed that the ion size parameter of chloride ions have the value of 1.5 at every temperature and in all selected buffers. For a measurement of pH with cell (I) to be traceable to the SI, an uncertainty for the Bates-Guggenheim convention must be estimated. One possibility is to estimate a reasonable uncertainty contribution due to a variation of the ion size parameter. An uncertainty contribution of ± 0.01 [10] in pH should cover the entire variation. When this contribution is included in the uncertainty budget of a primary pH standard, the uncertainty at the top of the traceability chain is inappropriately high to derive secondary standards as used to calibrate pH meter-electrode assemblies. For most measurement results the contribution due to the Bates-Guggenheim convention will therefore not be taken into account.

National metrology institutes (NMIs) use this conventional primary measurement procedure to assign pH(PS) values to Primary Standards in dilute aqueous solutions between pH 3 and 10 and in a temperature range from 5 to 50°C.

3.2 Primary pH standard reference buffers

Primary pH standard buffer materials are selected to be available at high purity, to have a long time stability and a good reproducibility of preparation [10]. Apart from the applicability of Bates-Guggenheim the buffer solutions prepared from these materials have small dependence on temperature $0.001 - 0.01 \text{ K}^{-1}$. The pH(PS) values do not include any diffusion potentials. The primary buffer solutions have been selected so that only small diffusion potentials occur in measurements made with pH electrodes incorporating free flow liquid junctions. The order of the residual liquid junction potential occurring using commercial electrodes of course depends on the kind of liquid junction device (e.g. sleeve, single pore, platinum, ceramic) used.

Further attributes of the primary pH standards are a high buffer capacity and a low dilution effect [19]. Figures are given in the German standard DIN 19261 [31].

Each batch of material must be certified. For solid material a description on how the buffer solution has to be prepared is part of the calibration certificate. The pH and the associated uncertainty for a batch are given in the certificate together with the measurement temperature.

In table 1 typical values of the pH (PS) of primary standard reference buffer solutions are listed.

These are examples taken from the DIN 19266 [11]. The figures should not be used in place of the certified value for a specific batch of buffer material.

Table 1. Typical values of pH(PS) for primary standards at 25°C. The figures should not be used in place of the certified value for a specific batch of buffer material.

Primary pH standard reference buffers	Molality in mol kg ⁻¹	pH (PS), typical values at 25°C [20]
Potassium hydrogen tartrate	Saturated at 25°C	3.557
Potassium dihydrogen citrate	0.05	3.775
Potassium hydrogen phthalate	0.05	4.008
Potassium dihydrogen phosphate /disodium hydrogen phosphate	0.025/0.025	6.865
	0.008695/0.03043	7.416
Sodium tetraborate decahydrate	0.01	9.182
Sodium bicarbonate /sodium carbonate	0.025/0.025	10.014

A typical expanded uncertainty for a determination of pH(PS) using cell(I) is $U = 0.003$ (coverage factor, $k=2$) at 25°C. The batch to batch variations are of the same order.

Calcium hydroxide and potassium tetraoxalate are not longer recommended by IUPAC as primary buffers because the contribution of the hydroxyl or hydrogen ion to the ionic strength is significant. For calcium hydroxide the preparation of the standard reference material is also extremely time consuming and consists of several steps[12].

3.3. Secondary standards and secondary methods for pH measurement

Secondary pH reference materials can be derived by different measurement procedures. Using evaluated uncertainties, it is possible to rank primary and secondary reference materials in terms of the methods used for their pH determination. The choice between the methods should be made according to the target uncertainty required for the application.

For the highest metrological quality it is strongly recommended to derive secondary standards from primary standards of nominally the same chemical composition. Liquid junction potentials are largely minimised when buffer solutions of nominally the same chemical composition are separated from each other in a strictly isothermal differential potentiometric cell (II) containing two platinum hydrogen cells at exactly the same hydrogen pressure [13]. The liquid junction device, is preferably a glass disk of fine porosity. Under these conditions, the contribution of the liquid junction potential to the cell voltage and therefore the increase in uncertainty of pH(SS) compared to pH(PS) is very small.

Pt,H₂ | primary buffer, pH (PS) || secondary buffer, pH (SS), Pt,H₂ cell (II)

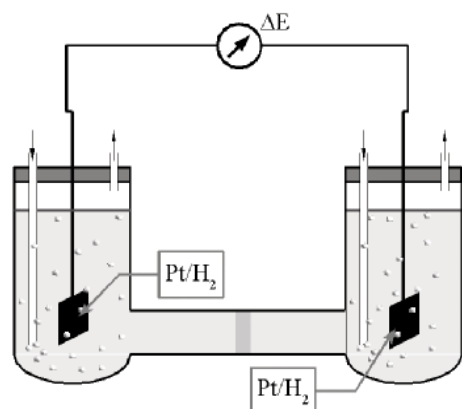


Figure 2. Schematic design of a differential potentiometric cell.

3.4. Secondary standards derived from measurements in cell (I)

Buffer material that do not fulfil all the criteria for primary pH reference materials but to which pH values can be assigned using cell (I) are considered also to be secondary pH standards, pH(SS).

An example for such a secondary buffer is acetic acid for which it is difficult to achieve consistent chemical quality. Also the zwitterionic buffers [14] (e.g. HEPES and MOPSO) and the nitrogen bases of the type BH^+ (e.g. (TRIS, tris-hydroxymethyl aminomethane) are excluded to be primary pH reference materials because either the Bates-Guggenheim convention is not applicable, or the liquid junction potentials are high. It is possible to link the pH(SS) values to the primary pH standards by comparison measurements using a cell with two free liquid junctions [15]. This cell is hard to realize. It will be a task of future work to link these standards with low uncertainty to the primary ones.

The Bates-Guggenheim convention has a limited validity to ionic strengths $I \leq 0.1 \text{ mol kg}^{-1}$. For applications in clinical chemistry and environmental samples traceable pH standard with ionic strengths more similar to the samples would be lower the liquid junction potentials in practical measurements and could improve the comparability of measurement results.

To overcome the current limitations for the primary pH standards and to extent to standards to higher ionic strength investigations into solution theory and into the concept of single ion activity are necessary.. One approach is to investigate the potential of the Pitzer model of electrolytes [16],[17],[18], which uses a virial equation approach to provide an improvement in the primary method. Also for the Pitzer equation the uncertainty of all components have to be estimated [17].

3.5.. Calibration of pH meter-electrode assemblies

Routine pH measurements are carried out using pH meter-glass electrode assemblies. In most cases the glass and reference electrodes are thereby fashioned into a single probe, the so-called 'combination electrode' or simply 'the pH electrode'. Using these electrodes, various effects producing uncertainties of unknown magnitude must be noted [19]. Therefore the measurement of pH of a sample requires a suitable calibration by certified standard buffer solutions (CRMs) traceable to the primary and secondary pH standards.

According to the number of standards used the calibration procedures can be subdivided into:

- single-point calibration
- two-point calibration
- multi-point calibration

The single-point calibration is carried out on only one CRM, the calibration result consists of only one parameter, the intercept of the pH versus potential function resulting in the practical slope factor is assumed to have the same value as the theoretical (Nernst) slope factor.

In most routine applications, glass electrode cells are calibrated by the two-point or bracketing procedure, using two CRMs with values that „bracket“ the range in which the sample pH lies. The multi-point calibration [20] is recommended if minimum uncertainty and maximum consistency are required over a wide range of unknown pH values. This calibration procedure is also recommended for characterising the performance of electrode systems.

4. Traceability chain for pH in Germany

In Germany laboratories accredited by the German Calibration Service (DKD) for the quantity pH use the cell (II) to derive secondary standards pH standard reference buffer from the primary ones. The multi-point calibration procedure is applied to derive technical buffer solutions or so-called ready-to use buffers as CRMs from secondary pH standards.

For several years a traceability chain for pH measurements has been established within the German measurement infrastructure. Calibration laboratories accredited by the DKD have an

intermediate multiplier function in disseminating traceable references materials for calibration of pH meter electrode assemblies. The users could be sure that the reference buffers they buy are certified and traceable to national standards. Accreditation by the DKD is international due to the mutual agreement between the members of the European Cooperation for Accreditation and bilateral agreements between specific countries.

The traceability chain for pH established within the German measurement infrastructure is illustrated in figure 3.

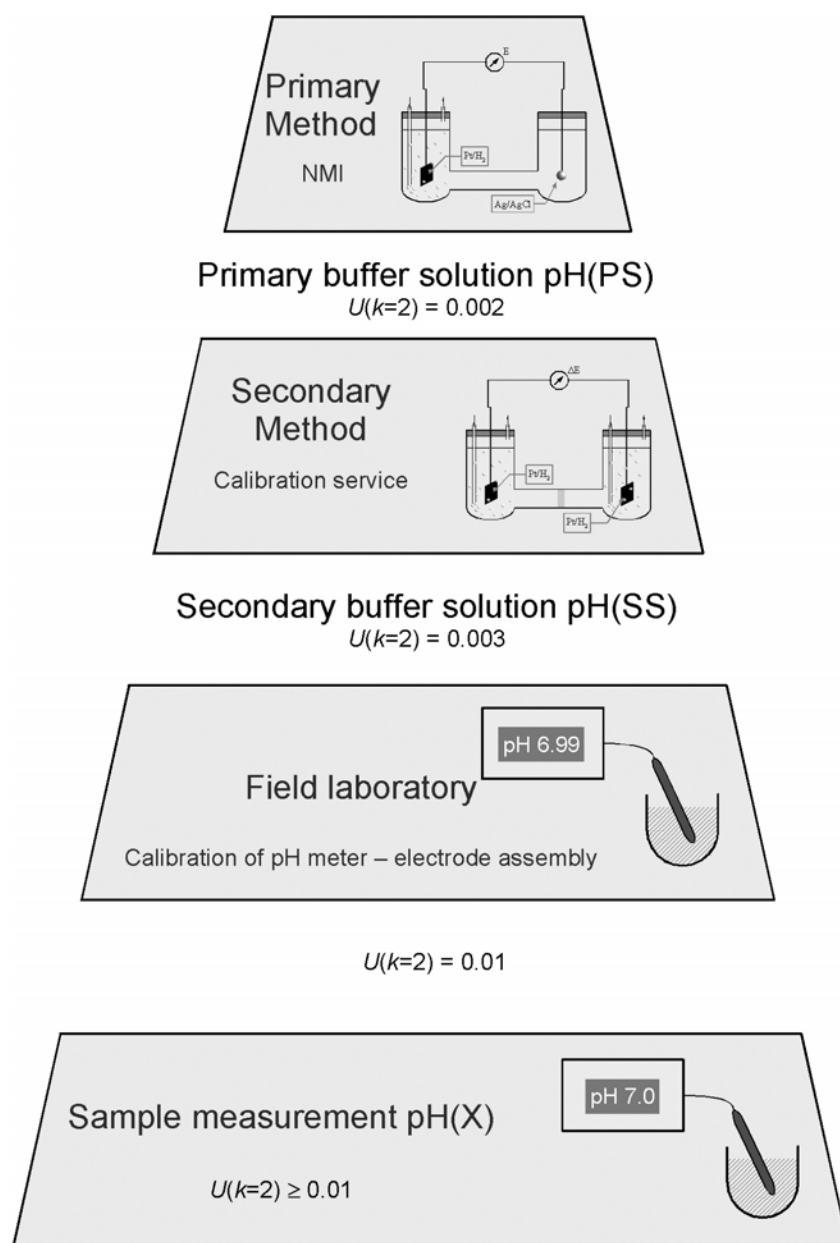


Figure 3. Traceability chain for pH as realized in Germany

5. International key comparison on the primary method for pH

The degree of equivalence of the primary standards for pH measured at different NMIs is established by the Mutual Recognition Arrangement (MRA) [21] for national measurement standards and for calibration and measurement certificates issued by national metrology institutes in 1999.

To support the MRA the first key comparison for pH, CCQM-K9 [22], was organised by the CCQM (Consultative Committee for Amount of Substance of the BIPM in Paris) in 2000 on two phosphate buffer solutions. A second key comparison on a phthalate buffer solution (CCQM-K17) started in 2001.

The key comparison CCQM-K9 was co-ordinated by the CCQM Working Group on Electrochemical Analysis and piloted by the Physikalisch-Technische Bundesanstalt (PTB) with assistance from the Slovak Institute of Metrology (SMU) and the National Institute of Standards and Technology (NIST).

A high degree of agreement of the measurement results of the NMIs is evident. The majority of the results obtained agree within the uncertainty stated by the ten participants.

Two phosphate buffers, both containing potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) at different molalities were chosen as transfer standards. The molality ($\text{mol}\cdot\text{kg}^{-1}$) was known to the participants only for sample (1).

Sample (1): $0.025 \text{ mol}\cdot\text{kg}^{-1} \text{KH}_2\text{PO}_4 + 0.025 \text{ mol}\cdot\text{kg}^{-1} \text{Na}_2\text{HPO}_4$

Sample (2): $0.02 \text{ mol}\cdot\text{kg}^{-1} \text{KH}_2\text{PO}_4 + 0.02 \text{ mol}\cdot\text{kg}^{-1} \text{Na}_2\text{HPO}_4$

It was recommended to the participants of CCQM-K9 to carry out the measurements between 5°C and 50°C in steps of 5°C , but at least at 15°C , 25°C and 37°C , because not all were able to measure in the whole temperature range.

As the method of choice for the determination of the molality of HCl coulometric titration was recommended as a primary method.

The evaluation of CCQM-K9 confirms the results obtained in the comparisons which performed under EUROMET co-operation, which have demonstrated the comparability of measurements within $\Delta\text{pH} = 0.005$ in different laboratories using samples from a single batch [23], [24], [25].

The uniformity of the results obtained with sample (1) with known molality was negligibly better than the uniformity of sample (2) with unknown composition. This confirmed the competence of the participants.

As an example the results for sample (2) at 25°C are given in table 3 and illustrated in figure 4

Table 3. pH values for sample (2) of the key comparison CCQM-K9: $0.02 \text{ mol}\cdot\text{kg}^{-1} \text{KH}_2\text{PO}_4 + 0.02 \text{ mol}\cdot\text{kg}^{-1} \text{Na}_2\text{HPO}_4$ at 25°C .

Participant	pH	Expanded uncertainty $U(k=2)$
1	6,8877	0,0016
2	6,8886	0,0040
3	6,8896	0,0018
4	6,8903	0,0016
5	6,8914	0,0022
6	6,8923	0,0016
7	6,8933	0,0084
8	6,8936	0,0036
9	6,8941	0,0042
10	6,9066	0,0130

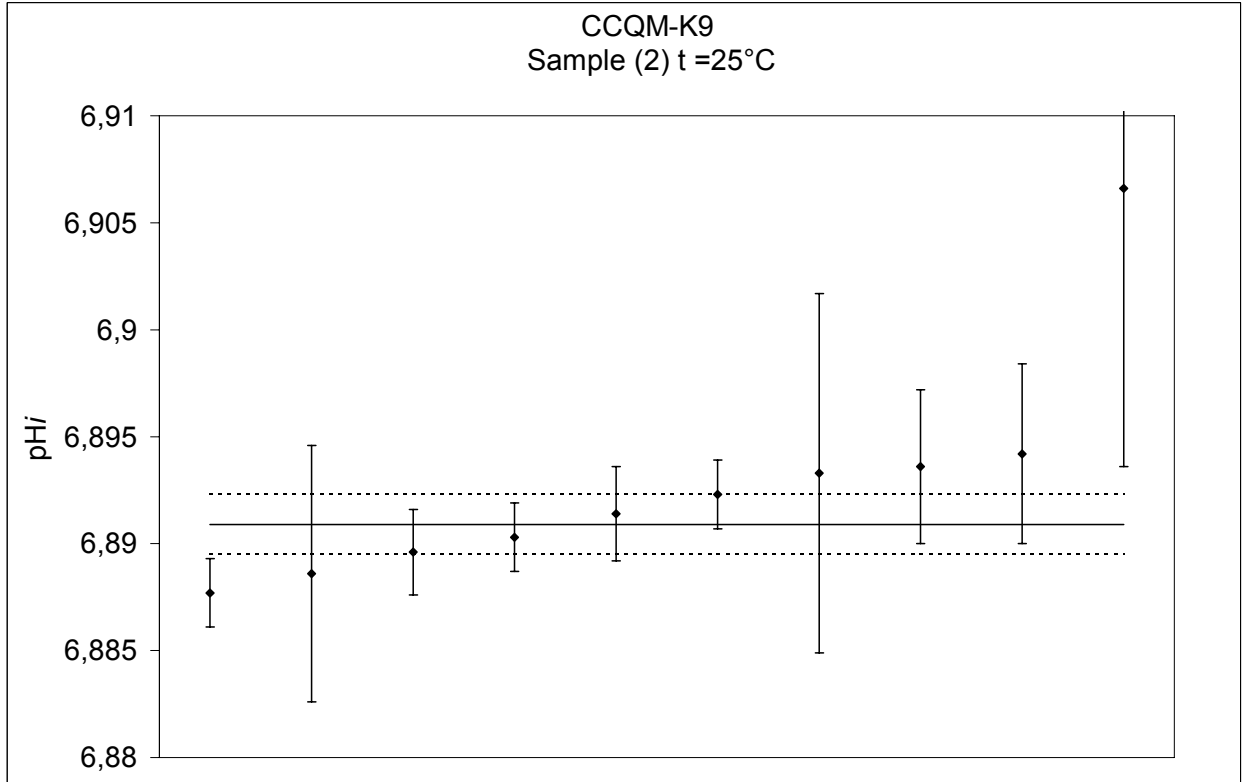


Figure 4. Results for sample (2) in the CCQM-K9 key comparison on pH
The key comparison reference value - and its expanded uncertainty -- (coverage factor $k = 2$)

The value provided by each laboratory is considered as an unbiased estimate of the quantity of concern [26]. The maximum-likelihood estimator yields the key comparison reference value (KCRV, pH_R , as the variance based weighted mean [27] according to equations (2), (3) and (4).

$$\text{pH}_R = \frac{\sum_{i=1}^N w_i \text{pH}_i}{\sum_{i=1}^N w_i} \quad (2) \quad w_i = \frac{C}{u_i^2} \quad (3) \quad C = \frac{1}{\sum_{i=1}^N \frac{1}{u_i^2}} \quad (4)$$

where pH_i represent the individual results and w_i : the individual weights.

The values of u_i are the individual uncertainties and C is the variance. According to equation (2) the KCRV at 25°C is $\text{pH}_R = 6.8909$.

A reasonable estimate of the uncertainty for the KCRV is that of the external consistency concept [28] taking into account the individual uncertainties and the spread of the results according to equation (5). The uncertainty for the KCRV at 25°C is therefore $u'(\text{pH}_R) = 0.00070$ ($k = 1$).

$$u'(\text{pH}_R)^2 = \frac{\sum_{i=1}^N (w_i (\text{pH}_i - \text{pH}_R)^2)}{(N-1) \cdot \sum_{i=1}^N w_i} \quad (5)$$

6. Conclusion

The key to higher reliability of measurement standards is demonstrated traceability to international recognised references. The first key comparison on pH which was organised in the framework of CCQM demonstrated a high degree of equivalence of the national measurement standards for pH. Within the Mutual recognition agreement MRA, linking the national metrology institutes, the measurement competence of the laboratories at the top of the traceability chain will be continuously demonstrated by key comparisons.

Numerous national and international standards on pH are still applicable. Following the increasing demands for quality assurance in laboratories, a European standard in this field was needed. In 1999, a Working Group on Instrumentation in Electrochemical Analysis (WG 5) was created by the Technical Committee Laboratory Equipment of the European Committee for Standardisation (CEN/TC 332). It is clearly stated that this standardisation work will not duplicate the work already completed by IUPAC or by IEC (International Electrotechnical Commission). This European standard addresses on its first line the needs of manufacturers of pH meters, pH electrodes, and of pH standards as well as of calibration laboratories and end-users like test laboratories as a basis for performing pH measurements. The CEN standard will consist of three parts dealing with general aspects and terminology, certification of reference materials for pH measurements, calibration of pH measuring equipment and practical pH measurements.

The uncertainty budget for a sample pH must taken into account the uncertainties of the certified reference buffer solutions used to calibrate the pH meter-electrode assembly as well as the uncertainties from the operation of the measurement procedure.

When uncertainty is evaluated according to the principles of the Guide to the Expression of Uncertainty in Measurement (GUM) [29] it is given as an interval around the result of the measurement. The interval expressing the uncertainty of the result enable the “fitness for purpose” of a result to be judged. It becomes also obviously if the upper or lower limit of the measurement uncertainty is close to or beyond a legal limit [30].

There is hope that the concept of traceability for pH measurement will also influence the numerous application notes for pH measurements in different matrices. The traceability of pH measurements for application in fundamental and applied science must be disseminated to field laboratories. A pH value given without any uncertainty and without measurement temperature is meaningless.

It has been demonstrated that the required comparability of pH and hence acceptance of measurement results can be improved if the certified reference solutions used for the calibration of pH meter-electrode assemblies are traceable to recognised primary references.

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