Anal Bioanal Chem (2002) 374 : 778–786
DOI 10.1007/s00216-002-1506-5

SPECIAL ISSUE PAPER

R. Naumann · Ch. Alexander-Weber · R. Eberhardt
J. Giera · P. Spitzer

Traceability of pH measurements by glass electrode cells: performance characteristic of pH electrodes by multi-point calibration

Received: 10 April 2002 / Revised: 27 June 2002 / Accepted: 11 July 2002 / Published online: 20 September 2002

Abstract Routine pH measurements are carried out with 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'. The use of these electrodes is subject to various effects, described below, producing uncertainties of unknown magnitude. Therefore, the measurement of pH of a sample requires a suitable calibration by certified standard buffer solutions (CRMs) traceable to primary pH standards. The procedures in use are based on calibrations at one point, at two points bracketing the sample pH and at a series of points, the so-called multi-point calibration. The multi-point calibration (MPC) is recommended if minimum uncertainty and maximum consistency are required over a wide range of unknown pH values. Details of uncertainty computations for the two-point and MPC procedure are given. Furthermore, the multi-point calibration is a useful tool to characterise the performance of pH electrodes. This is demonstrated with different commercial pH electrodes.
Electronic supplementary material is available if you access this article at http://dx.doi.org/10.1007/s00216-002-1506-5. On that page (frame on the left side), a link takes you directly to the supplementary material.

Keywords Metrology · pH · Measurement traceability · Measurement uncertainty

Introduction

The measurement of pH, although dealing with one of the most frequently determined physicochemical quantities, is still not satisfactorily established despite the long-standing efforts devoted to its determination [1] . The new IUPAC (International Union of Pure and Applied Chemistry) recommendation on the measurement of pH [2] overcomes some of the existing difficulties by introducing metrological concepts. According to this recommendation, pH values measured can be traced back to recognised references which are related to the thermodynamic definition of the pH. However, in its present form, the new IUPAC recommendation on the measurement of pH focuses on the primary and secondary level of pH measurement. Measurement procedures at this level mainly are used at National Metrology Institutes, like PTB (Physikalisch-Technische Bundesanstalt) in Germany or NIST (National Institute for Standards and Technology) in the United States and to calibration laboratories establishing pH standards. Procedures to derive certified reference buffer solutions different in composition from the primary standards as well as calibration procedures are treated not in detail. Thus, the new IUPAC recommendation has to be further extended to the application level. The present communication deals with the assessment of calibration procedures, the multi-point calibration (MPC) in particular, of pH electrodes thereby using certified reference buffer solutions (CRMs) traceable to primarypH standards. Attention is focused on the assignment of measurement uncertainties to CRMs like ready-to-use buffer solutions frequently in use for the calibration of pH electrodes. The incorporation of the uncertainty not only for the primary level, but also for all subsequent measurements, permits the uncertainty for all procedures to be linked to the primary pH reference materials by an unbroken chain of comparisons. Thus, pH values become traceable to internationally recognised references.

It will be shown that the unavoidable development of liquid junction potentials at the contact of the measuring

---

Electronic supplementary material is available if you access this article at http://dx.doi.org/10.1007/s00216-002-1506-5. On that page (frame on the left side), a link takes you directly to the supplementary material.

R. Naumann
Max Planck Institute of Polymer Research,
Ackermannweg 10, 55128 Mainz

Ch. Alexander-Weber
Merck KgaA, Frankfurter Str. 250, 64293 Darmstadt

R. Eberhardt · J. Giera · P. Spitzer (✉)
Physikalisch-Technische Bundesanstalt,
Bundesallee 10, 38116 Braunschweig
e-mail: petra.spitzer@ptb.de

solution and the reference electrode filling solution can be held responsible for a major contribution to the measurement uncertainty of a pH measurement result. The influence of different liquid junction devices on the pH measurement is studied by using six different commercial electrodes with different junction design, such as capillary, sleeve, platinum or ceramics. Furthermore, multipoint calibration is shown to be a useful tool to characterise the performance of pH electrodes. Examples illustrate the evaluation of the measurement uncertainty for the different calibration procedures.

Sources of uncertainties of pH measurements made with pH meter-glass electrode assemblies

The pH measuring set-up

A pH measuring set-up comprises a pH meter, a temperature sensor and a glass electrode together with a reference electrode, mostly designed as a combination or single rod pH electrode. The pH electrode is illustrated schematically in Fig. 1 and can also be represented by the cell equation (1)

$$\begin{aligned}&\mathrm{Ag|AgCl|KCl(3.5M)}\vdots\,\mathrm{buffer_{sample}|glass|}\\&\mathrm{reference\ buffer_{pH=7}}\vdots\,\mathrm{KCl(3.5M)|AgCl|Ag}\end{aligned}\qquad(1)$$

As shown in Fig. 1 as well as in cell equation (1), the probe contains the internal reference electrode and the internal reference electrolyte, the reference buffer, the glass membrane as well as the (external) reference electrode and reference electrolyte (generally 3.5 mol L^{-1} potassium chloride solution).

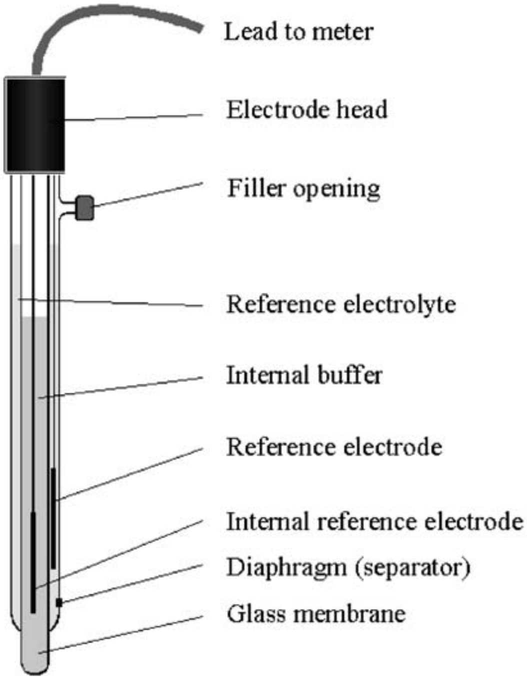

Fig. 1 Schematic construction plan of a pH combination electrode

Two liquid junctions are involved, given by the symbol $\vdots$. The first liquid junction is connecting the inner reference element to the inner reference buffer solution; the second one connects the reference electrode to the sample solution, denoted as $\mathrm{buffer_{sample}}$ in the cell equation. Obviously it is the latter whose junction potential varies when the sample solution is exchanged for another sample or a calibration buffer, whereas that of the former junction remains the same. Liquid junction devices (diaphragms) most frequently used to connect the reference electrode to the sample are:

(i) capillaries
(ii) so-called Pt junctions (actually a bundle of Pt wires)
(iii) ceramics
(iv) fibre junctions
(v) glass sleeve

Calculations of liquid junction potentials usually refer to linear concentration profiles between connecting solutions [3, 4]. Such profiles can be verified only in capillary junctions of the free-flowing type [1], which can hardly be realised in commercial electrodes. Complex concentration profiles are difficult to take into account by numerical simulation, if not impossible. The geometry may also vary with the individual specimen of the junction. Hence, an experimental approach to the liquid junction potential would be highly desirable. The problem is that liquid junction potentials cannot be measured independently. Differences between them, however, can be detected by comparison measurements with pH electrodes of different commercial origin.

Output parameters of the pH electrode

The pH electrode output is a potential difference measured between the inner reference system of the glass electrode and the outer reference electrode. This potential difference is a function of the pH and temperature of the solution to be measured. The potential of the reference electrode remains constant.

Output parameters are the slope and the intercept of the pH versus potential function, defined further below. The intercept also termed $\mathrm{pH_0}$ is usually close to pH 7 as long as the pH of the internal buffer solution is also close to pH 7 [5].

Sources of uncertainties of pH measurements

Measurements with pH electrodes are affected by various random and systematic effects, as specified in the IUPAC document [2]:

i) The glass electrode exhibits a slope of the cell potential versus pH function smaller than the theoretical Nernst slope of 59.16 mV at 25 °C [6].
ii) The response of the electrode may be affected by such effects as history of use, stirring and clogging.

iii) Individual response times of the electrodes [7], that is the time until the electrode potential reaches a stationary value, may vary with time.
iv) The potential of the glass electrode and to a lesser extent also the potential of the reference electrode are temperature dependent.
v) As mentioned above, the liquid junction device causes an individual device-dependent liquid junction potential.
vi) The liquid junction potential varies with the composition of the solution forming the junction.
vii) Uncertainty of the pH(S) value of the CRM used for calibration contributes to the overall uncertainty of the measurement.

This report deals with the following question: how can these effects be taken into account by a reasonable uncertainty budget for the calibration and measurement of pH with commercial pH meter-electrode assemblies? The electronic supplementary material provides detailed discussion of two examples.

Calibration

It is strongly recommended that calibration and measurement are performed under the same experimental conditions as the sample measurement. This includes same temperature, stirring conditions and response time.

One-point calibration

The one-point calibration is carried out on only one CRM; the calibration result consists of only one parameter, that is the intercept of the pH versus potential function, whereas the practical slope factor is assumed to have the same value as the theoretical (Nernst) slope factor k or as the practical slope factor k' which originate from a previous calibration. The one-point calibration could be used for certain applications if the last multi-point calibration is recent and if the pH value of the CRM and the pH value of the sample are very similar.

Two-point calibration

In the majority of practical applications, pH electrodes are calibrated by the two-point calibration or bracketing procedure, by using two CRMs with pH values pH(S_1) and pH(S_2) bracketing the sample pH(X) [8]. The respective potential differences measured are E_1, E_2 and E(X). The pH value of the unknown sample, pH(X), is obtained from Eq. (2).

$$\mathrm{pH}\,(\mathrm{X}) = \mathrm{pH}\,(\mathrm{S}_1) - \left(\frac{E\,(\mathrm{X}) - E_1}{k'}\right) \tag{2}$$

The result of the calibration consists of the two parameters: pH_0 (pH value for which the calibration line gives a cell potential (emf) of zero) and k' (practical slope of the electrode). These two parameters define the calibration line.

The practical slope factor k' is given by Eq. (3)

$$k' = \left(\frac{E_1 - E_2}{\mathrm{pH}\,(\mathrm{S}_1) - \mathrm{pH}\,(\mathrm{S}_2)}\right) \tag{3}$$

The pH corresponding to a zero potential reading, pH_0, is obtained from Eq. (4).

$$\mathrm{pH}_0 = \mathrm{pH}\,(\mathrm{S}_1) + E_1 \left|\frac{\mathrm{pH}\,(\mathrm{S}_1) - \mathrm{pH}\,(\mathrm{S}_2)}{E_1 - E_2}\right| \tag{4}$$

Uncertainties can be calculated according to standard procedures [9, 10]. Details are given elsewhere [11, 12]. A full report of an example calculation of the calibration parameters and unknown pH(X) including the uncertainty budget is given in the electronic supplementary material. The calculation of calibration parameters is usually part of the pH meter software; in some instruments the calibration parameters have to be entered manually and this operation is called adjustment.

As revealed by the example calculation, there are reasons why the two-point calibration is not designed to quantify all the uncertainties caused by the abovementioned deficiencies:

i) The calibration line given by pH_0 and k' incorporates all uncertainties mentioned above but it offers no possibilities to identify an outlying observation.
ii) To evaluate the uncertainty of the sample pH(X) it is necessary to make certain assumptions regarding all of the abovementioned uncertainty components. Quantitative information about these components is, however, available only from independent sources, for example standard deviations from independent measurements or from other experiences or otherwise from calculations or literature values. This is especially true for the liquid junction potential between the reference electrolyte of the pH electrode and the sample. As mentioned above, liquid junction potentials can neither be measured directly nor can they be easily calculated, particularly in the case of commercial devices.
iii) The two-point calibration results in different slopes of the calibration line and hence in different pH(X) values for one and the same given sample X depending on the choice of the two standards, as illustrated in Fig. 2.

Multi-point calibration

Inconsistencies encountered by the two-point calibration as described above are minimised if more than two standards are used for the calibration [8, 12]. The multi-point calibration (MPC) allows assessment of the uncertainty associated with an individual pH measurement by the statistical concept of OLS (ordinary least squares regression) [12]. MPC is recommended when minimum uncertainty

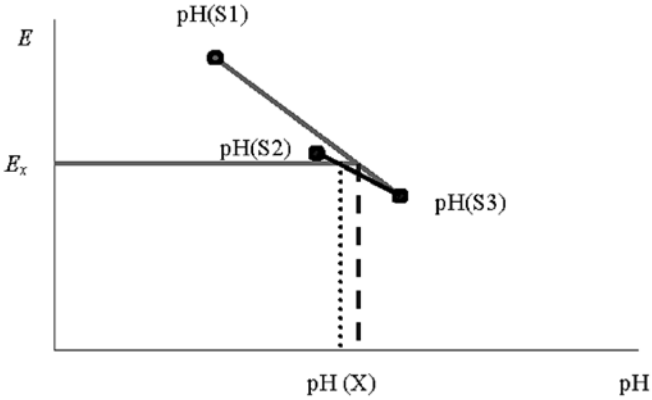

Fig. 2 Two-point calibration using different sets of standards pH(S)

and maximum consistency is required over a wide range of sample pH values. The OLS is applicable only to that range of pH values in which the calibration function is linear. Deviations from linearity are caused for example by the so-called alkali-error of the electrode. The necessary assumptions for OLS and more sophisticated concepts are described elsewhere [12]. Sophisticated concepts are necessary if there is any doubt on the linearity or if the uncertainty of the pH value of the CRM must be taken into account.

The assignment of a pH(X) to an unknown sample based on the MPC procedure by OLS as well as the associated uncertainty budget will be shown in the electronic supplementary material.

In MPC, the pH electrode is generally calibrated against five CRMs with pH(S_1) to pH(S_5) and the measured potential differences E(S_1) to E(S_5) are transferred into a calibration line by ordinary least squares (OLS). The use of more than five CRMs does not yield additional information [12]. The calibration function of the pH electrode represented by the cell equation (1) is then given by Eq. (5):

$$E\,(\mathrm{S}) = -E^{0\prime} - k'\mathrm{pH}\,(\mathrm{S}) \tag{5}$$

To fulfil the assumption that the uncertainty associated with the CRMs can be neglected the stated expanded uncertainty [9][1] of the pH(S) should be $U \leq 0.006$ (coverage factor k=2). Then the assumption is justified that errors are mainly present in the ordinate values so that ordinary linear regression can be applied to obtain the standard potential difference, E^{0}', and the *practical* slope factor *k*'. The value of *k*' is given by Eq. (6).

$$k' = \frac{dE\,(\mathrm{S})}{d\,(\mathrm{pH}\,(\mathrm{S}))} \tag{6}$$

k' is smaller than *k*, the *theoretical s*lope (Nernst) factor. Consequently, the ratio β=*k*'/*k* denoted the electromotive efficiency of the pH glass electrode, is smaller than unity [6, 11].

The calibration line is then used to obtain pH(X) from the potential difference, *E*(X), by using Eq. (7):

$$\mathrm{pH}\,(\mathrm{X}) = \frac{-E^{0\prime} - E\,(\mathrm{X})}{k'} \tag{7}$$

An estimate of the standard uncertainty of the sample pH(X) can be obtained directly from the calibration data. Additional information obtained by the regression procedure are the uncertainties of the slope, *k*', and the intercept, E^{0}'. Hence multi-point calibration is designed to quantify the deficiencies of the pH measurement by combination glass electrodes listed above, since it supplies comprehensive information about the parameters of the calibration function and their uncertainties directly from the experimental data. Consequently, multi-point calibration is recommended when minimum uncertainty and maximum consistency are required over a wide range of pH values.

Results and discussion

Measurements with different kinds of commercial electrodes

The first series of measurements was carried out with commercial pH electrodes of different origin. Electrodes differed in the type of glass, reference system and junction device. Four different types of liquid junction devices were employed: capillary, glass sleeve, Pt and ceramic plug. All measurements were carried out in the same ves-

Table 1 Secondary buffer solutions derived from primary buffers of the same chemical composition, expanded uncertainty of *U*(pH(S))=0.004

Buffer solution	Composition	Merck catalogue number	pH(S) (25 °C)
Oxalate (OX)	potassium tetraoxalate dihydrate, 0.05 mol kg^{-1}	101,961	1.681
Tartrate (TAT)	potassium hydrogen tartrate, 0.01 mol kg^{-1}	101,963	3.639
Phthalate (PHT)	potassium hydrogen phthalate, 0.05 mol kg^{-1}	101,965	4.005
Phosphate 1:1 (PHO)	potassium dihydrogen phosphate + disodium hydrogen phosphate, 0.025 mol kg^{-1}	101,960	6.863
Borate (BO)	sodium tetraborate decahydrate, 0.01 mol/kg^{-1}	101,964	9.184
Carbonate (CAR)	sodium hydrogen carbonate + disodium carbonate, 0.01 mol kg^{-1} each	101,962	10.014

---

[1] The expanded uncertainty *U* defines an interval about the result of the measurement. *U* is calculated from a combined standard uncertainty u_c and a coverage factor *k*: $U=ku_c$. A coverage factor *k*=2, as applied in the publication, corresponds for a normal distribution to a coverage probability of approximately 95%.

Table 2 Ready to use buffer solutions U (pH)=0.02

pH (25 °C)	Merck catalogue number
4.01	108,069
7.00	108,071
9.00	108,072

sel thermostated to 25±0.1 °C, equipped with synchronous stirring bar used at the same speed throughout. A pH meter with a resolution of 0.1 mV was employed equipped with a computer and software designed to follow the time course of the voltage reading. Readings were taken at a stability criterion of less than 0.1 mV min^{-1}. Individual response times of the electrodes [7] were thus taken into account. Calibration buffers were prepared in one batch each from CRMs, which were secondary standards of the same chemical composition as the respective primary standards specified in the IUPAC document as being characterised, inter alia, by low liquid junction potentials (<0.6 mV) and by low ionic strength (0.1 mol kg^{-1}). The pH(S) of these CRMs, listed in Table 1, were certified to have an expanded uncertainty of U(pH(S))=0.004.

Subsequent to the calibrations, the pH(X) of samples were measured which actually were ready to use buffer solutions (Merck Company) of pH ~4.00, 7.00 and 9.00; U (pH)=0.02 (25 °C) (Table 2).

Every data point was the mean value out of three replicates using different samples, thereby taking into account the standard deviation of the measurement as well as that of the sampling. The repeatability of the data points (standard deviation, not shown) was 0.2 mV or better, independent of the electrode and buffer solution employed, provided that the stability criterion mentioned above was properly chosen, so that readings were taken only after termination of the response time of the electrodes.

Evaluation according to the multi-point calibration

Data were collected, as shown in Table 3, on the basis of five calibration points. The parameters of the calibration line were calculated by OLS as described above, thereby obtaining the uncertainties of E^0, k' and pH_0. These uncertainties were combined to calculate the expanded uncertainties of the pH(X), U(pH(X)), according to the procedures given in the electronic supplementary material.

The consistency of the calibration line was tested by the so-called standard error of the estimate (SR). This is the square root of the residual mean square of the regres-

Table 3 pH(X) of three ready-to-use buffer solutions, measured with different electrodes, evaluated according to the multipoint calibration in the order of increasing uncertainty; U=expanded uncertainty; coverage factor k=2; u=standard uncertainty

Electrode	Reference system	Liquid junction device	pH(X)	U(pH(X))	E^0 (mV)	$u(E^0)$ (mV)	k' (mV)	$u(k')$ (mV)	pH_0	$u(\text{pH}_0)$	S_{x0}[b]	SR[a] (mV)
1	Ag/AgCl, KCl 3 mol L^{-1}	Capillary	4.022	0.020	426.66	0.25	58.93	0.04	7.24	0.0069	0.0044	0.26
			7.009	0.020								
			9.002	0.022								
2	thalamid	Pt	4.020	0.040	405.26	0.51	59.12	0.09	6.86	0.014	0.0090	0.53
			7.005	0.042								
			8.994	0.046								
3	Ag/AgCl, KCl 3 mol L^{-1}	Pt	4.025	0.042	408.08	0.54	58.94	0.1	6.92	0.014	0.0095	0.56
			7.005	0.044								
			8.997	0.048								
4	thalamid	glass sleeve	4.024	0.054	396.00	0.71	59.11	0.1	6.70	0.019	0.012	0.73
			7.009	0.056								
			8.995	0.064								
5	redox	ceramic	4.026	0.068	410.17	0.86	58.69	0.2	6.99	0.023	0.015	0.89
			7.025	0.070								
			9.018	0.074								
6	Ag/AgCl, KCl 3 mol L^{-1}	ceramic	4.004	0.090	410.44	1.15	58.55	0.2	7.01	0.031	0.020	1.18
			7.032	0.092								
			9.035	0.104								
7	Ag/AgCl, KCl 3 mol L^{-1}	ceramic	4.028	0.068	411.76	1.72	58.04	0.3	7.09	0.047	0.031	1.77
			7.053	0.070								
			9.049	0.039								

[a] *SR* standard error of the estimate = square root of the residual mean square; a measure of the spread of the residuals about the fitted line.
[b] S_{x0} method standard deviation [17] = *SR* divided by the slope (sensitivity) of the calibration line.

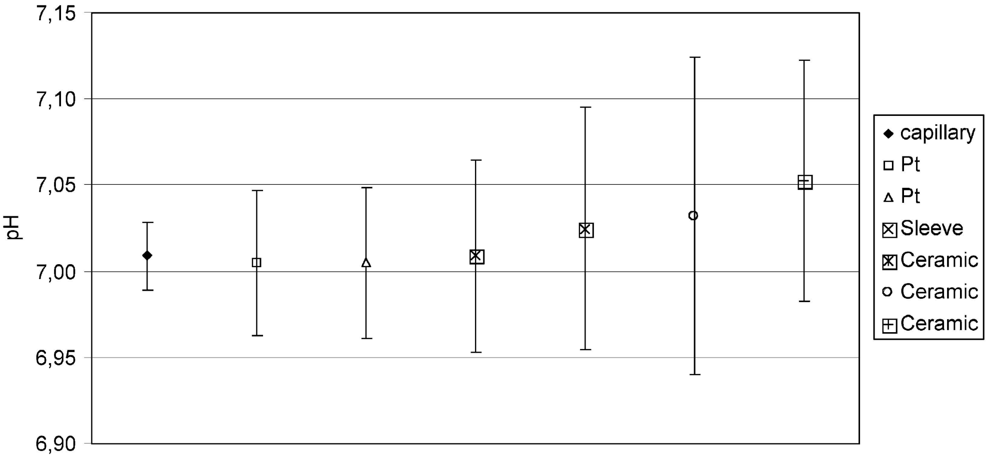

Fig. 3 pH(X), measured with different electrodes following a five-point calibration. The uncertainty given is the expanded uncertainty (coverage factor k=2). Sample is a ready-to-use buffer of pH ~7.00

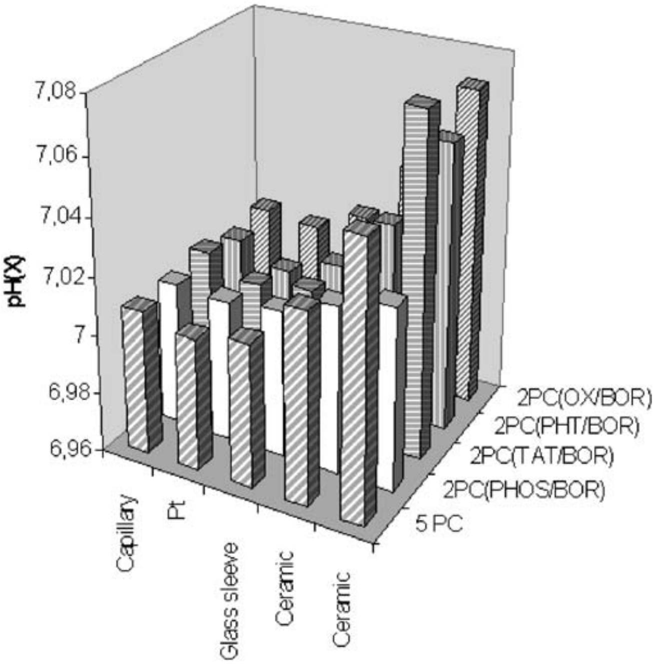

Fig. 4 pH(X) obtained with different pairs of calibration buffers

sion line representing the spread of the residuals about the fitted line. This SR value is shown in Table 3 to increase from top to bottom together with uncertainties of pH(X) and that of the parameters of the regression line.

As a result of Table 3, pH(X) values obtained are the same within the respective expanded uncertainty for all the electrodes tested. This also illustrated in Fig. 3 in the case of buffer pH 7.00 (25 °C) as unknown sample.

Differences, were obtained, however, regarding the expanded uncertainties of pH(X), E^0, k' and pH_0 increasing from top to bottom in line with the SR value. The lowest uncertainties are obtained with electrodes having capillary junctions, U(pH(X)) ~0.02, increasing to U(pH(X)) ~0.04 for electrodes equipped with Pt junctions. Uncertainties as high as U(pH(X)) ~0.09 were obtained with electrodes equipped with ceramic junctions. As far as glass sleeves are concerned, it should be mentioned that they were found to be of very variable quality and usually gave long response times compared to other devices. Hence, comparisons of uncertainties involved with those caused by other types of junctions are problematic, whereas junctions of the other designs used in this study were found to be of a more uniform quality, independent of the supplier.

In view of this sequence of uncertainties, specifications, for example in the case of ready-to-use buffers, were established to be U(pH(X))=0.02 on the basis of measurements with electrodes equipped with capillary junctions.

The results presented in Table 3 were found with numerous glass electrodes used over the years in several analytical laboratories to be typical for the respective liquid junction device, independent of the supplier, as mentioned above. Assuming that all the other influences on the uncertainty were kept constant or at least well controlled, we conclude that differences obtained for the different electrodes are mainly due to different liquid junction potentials.

Table 4 Comparison of different liquid junction devises. pH(X) of the unknown measured following the calibration by a different number and kind of buffer solutions. pH(X) = ready-to-use buffer (pH ~7.00), temperature 25 °C ; U is the expanded uncertainty (coverage factor k=2)

Liquid junction device	Capillary	Pt	Glass sleeve	Ceramic	Ceramic
Calibration method	pH(X)±U(pH(X))				
Five point calibration	7.01±0.020	7.01±0.044	7.01±0.056	7.03±0.092	7.05±0.070
Two point calibration	pH(X)±U(pH(X))				
PHOS/BOR	7.01±0.094	7.01±0.094	7.01±0.094	7.02±0.096	7.02±0.096
PHT/BOR	7.01±0.084	7.00±0.084	7.01±0.084	7.04±0.084	7.06±0.086
OX/BOR	7.01±0.086	7.01±0.086	7.02±0.086	7.05±0.086	7.07±0.088

Evaluation according to the two-point calibration

From the same set of measurements using CRMs of the same chemical composition as the respective primary standards, specified in Table 2, as well as the same set of electrodes used in Table 3, data were evaluated according to the two-point calibration. pH(X) obtained regarding buffer pH 7.00 as unknown sample, are presented in Fig. 4 employing different pairs of calibration buffers. pH(X) are shown to depend on the buffer pair used, particularly when electrodes equipped with ceramic junctions are employed. A similar result is also presented in Table 4, containing pH(X) including uncertainties obtained according to the multi-point and two-point calibration with different electrodes and different pairs of calibration buffers. Again in the case of the two-point calibration, pH(X) varies, within the expanded uncertainty U(pH(X))= 0.09 for all the electrodes tested. The uncertainty is based on example calculations given in the electronic supplementary material, estimating that the uncertainties of the potential readings, $E(S_1)$, $E(S_2)$ and E(X) due to the liquid junction potential are 2 mV each since no other specifications are available from the supplier. It can be shown by a similar calculation that U(pH(X)) does not change appreciably (to U(pH(X))=~0.07) even if we assume, as in the new IUPAC recommendation, that the standard uncertainties $u(E(S_1))$ and $u(E(S_2))$ due to the liquid junction potential of the two calibration buffers are only 0.6 mV as requested for primary standards. This underlines that the main contribution to the uncertainty of pH(X) is u(E(X)), the standard uncertainty of the potential reading of the sample itself.

According to these results, the largest deviations of pH(X) are obtained with electrodes equipped with ceramic junctions. This points to a common reason for the effect of shifting pH(X), schematically illustrated above in Fig. 4, namely the liquid junction potential (ljp).

Calibration with different kinds of secondary standards

CRMs used so far for calibration purposes were derived from primary standards of the same composition and thus have an expanded uncertainty of U(pH(S)) =0.004. Such standards are selected, inter alia, for their low liquid junction potentials (≤0.6 mV assuming free flowing junctions). There are other categories of secondary standards also in accordance with the new IUPAC recommendation, for example the so-called biological buffers (TRIS or tris(hydroxylmethyl)aminomethane and HEPES or *N*-(2-hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid) of a composition different from the primary standards. They do not meet the stringent criteria of the primary standards and therefore exhibit larger uncertainties, partly because larger liquid junction potentials are involved. The following set of measurements was designed to test the effect of such secondary standards on the result of pH measurements. Since these standards are not yet available as CRMs, their standard pH(S) were obtained from other sources, as indicated in the list of materials given in Table 5. Two different electrodes were used: one equipped with a capillary and one with a ceramic liquid junction device.

First of all, the set of five buffers used in above for the multi-point calibration was extended to eight calibration buffers including buffers of the second category. An increase in U(pH(X)) is not observed, as illustrated in Table 6, for both kinds of electrodes, showing that more than five standards do not improve the quality of the OLS. Also shown in Table 6 is the measurement of the pH(X) of TRIS and acetate as sample pH(X) evaluated according to the two-point calibration with different pairs of standards. Uncertainties are shown to be as high as U(pH(X))=0.1 to U(pH(X))=0.2, even with the capillary type of junction.

In the next series of measurements, two of the set of five buffers used in the multi-point calibration were replaced by secondary standards of the second category, acetate and TRIS. Results are collected in Table 7. Uncertainties are shown to increase appreciably together with the SR value particularly in the case of the capillary junction. Differences disappear when an electrode with a ce-

Table 5 Secondary standard buffer solutions with a composition different from the primary standards, expanded uncertainty of U(pH(S)=0.006

Buffer solution	Source	Composition	pH(S) (25 °C)	Notes
Citrate (CIT)	Merck KGaA	potassium hydrogen citrate, 0.05 mol kg^{-1}	3.776	Measured at PTB with a hydrogen electrode system (Harned cell)
TRIS[a] 1:3 (TRIS)	Merck KGaA	TRIS, 0.01667 mol kg^{-1} + TRIS-HCl, 0.05 mol kg^{-1}	7.699	
HEPES[b] 1:2(HEPES)	Merck KGaA	HEPES, 0.02 mol kg^{-1} + NaHEPES, 0.04 mol kg^{-1}	7.767	
Acetate (ACE)	Merck KGaA	acetic acid + sodium acetate, 0.1 mol kg^{-1} each	4.654	
Calcium hydroxide (CAHY)	Merck KGaA (cat. No.102111)	calclum hydroxide, satd. at 25 °C	12.45	Measured at Merck KGaA/LPRM with a differential potentiometric cell

[a]TRIS tris(hydroxylmethyl)aminomethane. [b]HEPES: *N*-(2-hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid.

Table 6 Comparison of different liquid junction devices. pH(X) of the unknown measured following a multipoint calibration by different kinds of buffer solutions. pH(X)=ready-to-use buffer (pH ~7.00), HEPES and acetate buffer ;*U* is the expanded uncertainty (coverage factor *k*=2)

Liquid junction device		Calibration procedure					
		5 calibration points	8 calibration points	8 calibration points	PHT/PHO	PHO/BOR	PHO/BOR*
Capillary	Sample	pH(X)±*U*(pH(X)), (expanded uncertainty, coverage factor=2)					
	Ready-to-use buffer pH~7.0	6.99±0.011	6.96±0.014	6.96±0.014		6.99±0.096	
	HEPES pH~7.77	7.77±0.011	7.74±0.014	7.74±0.014	7.77±0.14	7.77±0.12	7.77±0.19
	acetate pH~4.66	4.65±0.011	4.62±0.014		4.65±0.16	4.67±0.14	4.67±0.21
Ceramic	Sample	pH(X)±*U*(pH(X)), (expanded uncertainty, coverage factor=2)					
	Ready-to-use buffer pH~7.0	7.02±0.086	7.00±0.082	7.02±0.063	6.99±0.13	7.00±0.10	
	Hepes pH~7.77	7.77±0.088	7.75±0.082	7.77±0.064	7.74±0.13	7.74±0.13	7.77±0.19
	Acetate pH~4.66	4.68±0.090	4.67±0.082		4.58±0.13	4.66±0.15	4.66±0.21

Five calibration points: TAT, PHT, PHO, BOR, CAR. Eight calibration points: OX, TAT, CIT, PHT, PHO, BOR, CAR, CAHY. Eight calibration points: OX, TAT, CIT, PHT, PHO, BOR, CAR, ACE. Two points: PHT/PHO or PHO/BOR: assuming that the standard uncertainty *u* (*E*(pH(S))) and the standard uncertainty *u*(*E*(pH(X))) is estimated to 2 m.

Table 7 Comparison of the sample pH obtained with pH electrodes equipped with different types of liquid junction devices

pH(S)	Liquid junction device	Unknown	pH(X)	*U*(pH(X))	SR
OX, PHT, PHO, BOR, CAR	Capillary	ready to use (~4.01)	3.95	0.019	0.50
		ready to use (~7.00)	6.96	0.018	
		Tris (~7.67)	7.62	0.018	
OX, PHT, PHO, BOR, CAR	Ceramic	ready to use (~4.01)	3.99	0.078	2.00
		ready to use (~7.00)	7.01	0.074	
		Tris (~7.77)	7.66	0.076	
ACE, Hepes,PHOS, TAT, BOR	Capillary	ready to use (~4.01)	3.96	0.038	0.91
		ready to use (~7.00)	6.96	0.034	
		Tris (~7.67)	7.63	0.034	
ACE, Hepes,PHOS, TAT, BOR	Ceramic	ready to use (~4.01)	3.99	0.082	2.02
		ready to use (~7.00)	7.03	0.076	
		Tris (~7.67)	7.68	0.076	

ramic junction is used where larger uncertainties are involved anyway.

In summary, overall uncertainties become larger, as expected, when calibrations are performed with secondary standards of the second category.

Conclusions

We have demonstrated that liquid junction potentials may be significant in pH measurements using commercial pH meter glass electrode assemblies. A useful test in this respect has proved to be the multi-point calibration. Uncertainties obtained from the quality of the OLS are indicative of differences in the liquid junction potential over a large range of pH values. The multi-point calibration can thus be recommended as a performance characteristic of the pH electrode if it comes, for example, to the selection of an electrode proper for a particular application.

For the two-point calibration it is difficult to estimate the standard uncertainty caused by the liquid junction potentials. To be able to calculate a realistic measurement uncertainty, it would be highly desirable to obtain the necessary information from the supplier.

In summary, our results may be useful to obtain a better estimate of the uncertainty of routine pH measurements.

Significance of uncertainty considerations on the working level

In the majority of applications it may be sufficient to perform a pH measurement with an expanded uncertainty of *U*(pH(X))=0.5. Such an uncertainty level is easy to achieve, as shown by our measurements. It could be argued that in routine analysis it is not necessary to estimate all uncertainty components and to trace these pH measurements back to CRMs of stated uncertainty. Contrary to this argument, the complete knowledge of the uncertainty is the prerequisite for the comparability of the measurement and therefore for the reliability of the pH values. To quantify the measurement uncertainty, it is necessary to identify the sources of uncertainty in calibration and measurement and to quantify the uncertainty arising from these sources. This includes the measurement conditions, the type of electrode and meter used. In most cases, information about the magnitude of the liquid junction potentials is not available, particularly regarding the junction potential caused by the sample solution. Therefore, for the sake of comparability of the results, it is essential to keep the influence of the liquid junction potential constant. Suppliers of electrodes could well contribute to this requirement. In addition to these average types of applications, there are also cases, occurring with somewhat lower frequency, in which uncertainties as low as 0.02 are significant for pH measurement results. One example would be the examination of pH-dependent thermodynamic data. The laws of thermodynamics in solution operate much under the same conditions and for the same reasons as those valid for the primary standards, for example validity of ion activity concepts, concentrations below 0.1 mol kg^{-1}, choice of the solvent, temperature limitations etc. Hence in these cases, the effect of liquid junction potentials can be expected to be of the same order of magnitude as in the calibration examples presented above. Therefore, pH values should be traceable within these narrow limits to the primary standards and hence to the definition of pH [1] in the framework of thermodynamics. This is certainly significant as has been demonstrated, for example by calculations on the effect of the uncertainty of the pH value on species analysis with a large impact on environmental problems, for example species analysis of radionuclides [13, 14]. Other examples are equilibrium data such as pK values or stability constants of a complex. They also have to be known within very narrow limits considering their impact on many kinds of biochemically and pharmacologically significant processes.

Another case is buffer solutions used as calibration buffers with integer pH values, specified to within 0.02 pH units. For the sake of comparability and reliability of data and also for purposes of consistency over the entire range of pH values, it is necessary to trace back these CRMs to primary standards to within U(pH(X)=0.02. This should be done by the multi-point calibration [15, 16]. Otherwise, the specification would be obsolete. Moreover, it is recommended to use only CRMs with an uncertainty stated in a certificate for calibration purposes of pH meters. Ultimately, they are the basis of all the numerous pH measurements carried out on a daily basis worldwide.

References

1. Bates RG (1981) Crit Rev Anal Chem 10:247–278
2. Buck RP, Rondinini S, Baucke FGK, Brett CMA, Camoes MF, Covington AK, Milton MJT, Mussini T, Naumann R, Pratt KW, Spitzer P, Wilson GS (2001) The measurement of pH – definition, standards and procedures. Report of the Working Party on pH. IUPAC Provisional Recommendation. http://www.iupac.org/reports/provisional/archives.html. Cited 9 April 2002
3. Harper HW (1985) J Phys Chem 89:1685
4. Bagg J (1990) Electrochim Acta 35:361–367; (1991) 37:719
5. Bach H, Baucke FGK, Krause D (2001) Electrochemistry of glasses and glass melts, including glass electrodes, chap 2. Springer Verlag
6. Baucke FGK(1994) Anal Chem 66:4519–4524
7. Buck RP, Lindner E (1994) Pure Appl Chem 66:2527
8. Naumann R, Baucke FGK, Spitzer P (1997) Spitzer P (ed) Traceability of pH measurement, lectures delivered at the 126th PTB Seminar, PTB-Report W-68, (Physikalisch-Technische Bundesanstalt, Braunschweig, 1997), Traceability of pH measurements to standard pH values and calibration of pH meter-electrode assemblies: recommended procedures and definitions, pp 38–51
9. Guide to the expression of uncertainty in measurement (1993) Published in the Name of BIPM, IEC, IFCC, ISO, IUPAC, OIML by ISO, Geneva
10. EURACHEM/CITAC (2000) Quantifying uncertainty in analytical measurement, 2nd edn
11. Baucke FGK, Naumann R, Alexander-Weber C (1993) Anal Chem 349:3244
12. Meinrath G, Spitzer P (2000) Mikrochim Acta 135:155–168
13. Meinrath G, Hurst S, Gatzweiler R (2000) Fresenius J Anal Chem 368:561–566
14. Meinrath G, Nitzsche O (2000) Isotopes Environ Health Stud 36:195–210
15. Bates DM, Watts DG (1988) Nonlinear regression analysis and its applications. Wiley series in probabilities and mathematical statistics. Wiley & Sons, New York, USA
16. Ebel S, Glaser E, Mohr H (1978) Fresenius Z Anal Chem 293:33–35
17. DIN 32645 (1994) Chemische Analytik, Nachweis- und Bestimmungsgrenze, ermittlung unter Wiederholbedingungen, Begriffe, Verfahren, Auswertung, Beuth Verlag