The Measurement of pH - Definition, Standards and Procedures

REPORT OF THE WORKING PARTY ON pH

R.P. Buck (Chairman), S. Rondinini (Secretary), A.K. Covington (Editor), F.G.K. Baucke, C.M.A. Brett, M.F. Camoes, M.J.T. Milton, T. Mussini, R. Naumann, K.W. Pratt, P. Spitzer, G.S. Wilson.

Abstract

The definition of a "primary method of measurement" (1) has permitted a full consideration of the definition of primary standards for pH, determined by a primary method (cell without transference, Harned cell), of the definition of secondary standards by secondary methods, and of the question whether pH, as a conventional quantity, can be incorporated within the internationally-accepted SI system of measurement. This approach has enabled resolution of the previous compromise IUPAC (1985) recommendations (2). Furthermore, incorporation of the uncertainties for the primary method, and for all subsequent measurements, permits the uncertainties for all procedures to be linked to the primary standards by an unbroken chain of comparisons. Thus a rational choice can be made by the analyst of the appropriate procedure to adopt to achieve the target uncertainty of sample pH. Accordingly this document explains IUPAC recommended definitions, procedures and terminology relating to pH measurements in dilute aqueous solutions in the temperature range 5-50 ^{o}C. Details are given of the primary and secondary methods for measuring pH and the rationale for the assignment of pH values with appropriate uncertainties to selected primary and secondary substances.

CONTENTS

Abbreviations used

BIPM Bureau International des Poid et Mesures, France
CRMs Certified Reference
EUROMET European Collaboration in Metrology (Measurement Standards)
NBS National Bureau of Standards, USA, now NIST
NIST National Institute of Science and Technology, USA

NMIs National Metrological Institutes
PS Primary Standard
LJP Liquid Junction Potential
RLJP Residual Liquid Junction Potential
SS Secondary Standard

1 Introduction and Scope

1.1 pH, a single ion quantity.
The concept of pH is unique amongst the commonly encountered physicochemical quantities listed in the IUPAC Green Book (3) in that, in terms of its definition (4),

$$pH = - \lg a_H$$

it involves a single ion quantity, the activity of the hydrogen ion, which is immeasurable by any thermodynamically valid method and requires a convention for its evaluation.

1.2 Cells without transference, Harned cells.
As will be shown in § 4, primary pH standard values can be determined from electrochemical data from the cell without transference using the hydrogen gas electrode, known as the Harned cell. These primary standards have *good* reproducibility and *low* uncertainty. Cells involving glass electrodes and liquid junctions have considerably *higher* uncertainties as will be discussed later (§ 5.1, 10.1). Using evaluated uncertainties, it is possible to rank reference materials as primary or secondary in terms of the methods used for assigning pH values to them. This ranking of primary (PS) or secondary (SS) standards is consistent with the metrological requirement that measurements are traceable with stated uncertainties to national, or international, standards by an unbroken chain of comparisons each with its own stated uncertainty. The accepted definition of traceability is given in § 12.5. If the uncertainty of such measurements is calculated to include the hydrogen ion activity convention (§ 4.6), then the result can also be traceable to the internationally accepted SI system of units.

1.3 Primary pH standards.
In § 4 of this document the procedure used to assign primary standard [pH(PS)] values to primary standards is described. The only method that meets the stringent criteria of a primary method of measurement for measuring pH is based on the Harned cell (Cell I). This method, extensively developed by R.G. Bates (5) and collaborators at NBS (later NIST) is now adopted in national metrological institutes (NMIs) world-wide, and the procedure is approved in this document with slight modifications (§ 3.2) to comply with the requirements of a primary method.

1.4 Secondary standards derived from measurements on the Harned cell (Cell I).
Values assigned by Harned cell measurements to substances that do not entirely fulfil the criteria for primary standard status are secondary standards(SS) [with pH(SS) values] and are discussed in § 8.1.

1.5 Secondary standards derived from primary standards by measuring differences in pH.
Methods that can be used to obtain the difference in pH between buffer solutions are discussed in § 8.2-8.5 of these recommendations. These methods involve cells that are practically more convenient than the Harned cell, but have greater uncertainties associated with the results. They enable the pH of other buffers to be compared with primary standard buffers that have been measured with a Harned cell. It is recommended that these are secondary methods and buffers measured in this way are secondary standards (SS) [with pH(SS) values].

1.6 Traceability.

This hierarchical approach to primary and secondary measurements facilitates the availability of traceable buffers for laboratory calibrations. Recommended procedures for carrying out these calibrations to achieve specified uncertainties are given in § 11.

1.7 Scope.
The recommendations in this Report relate to analytical laboratory determinations of pH of dilute aqueous solutions ($\leq$ 0.1 mol kg^{-1}) Systems including partially aqueous mixed solvents, biological measurements, heavy water solvent, natural waters and high temperature measurements are excluded from this Report.

1.8 Uncertainty estimates.
The Annex (§ 13) includes typical uncertainty estimates for the use of the cells and measurements described.

2 Activity and the Definition of pH

2.1 Hydrogen ion activity.
pH was originally defined by Sørensen in 1909 (6) in terms of the concentration of hydrogen ions (in modern nomenclature) as pH = - lg (c_H/c^o) where c_H is the hydrogen ion concentration in mol dm^{-3}, and c^o = 1 mol dm^{-3}. Subsequently (4), it has been accepted that it is more satisfactory to define pH in terms of the relative activity of hydrogen ions in solution

$$pH = - \lg a_H = -\lg (m_H\gamma_H / m^o) \qquad (1)$$

where a_H is the relative (molality basis) activity and γ_H is the molal activity coefficient of the hydrogen ion H^+ at the molality m_H , and m^o is the molality standard state exhibiting infinitely diluted behaviour. The quantity pH is intended to be a measure of the activity of hydrogen ions in solution. However, since it is defined in terms of a quantity that cannot be measured by a thermodynamically valid method, eqn.(1) can be only a *notional definition* of pH.

3 Traceability and Primary Methods of Measurement

3.1 Relation to SI System.
Since pH is not measured in terms of a fundamental (or base) unit of any measurement system, it has become common practice to regard pH measurements as being traceable to their definition. A more satisfactory alternative is now available, since it has been accepted that measurements of chemical properties can be incorporated within the internationally-accepted SI system of measurement if they can be traced to measurements made using a method that fulfils the definition of a "primary method of measurement" (1).

3.2 Primary method of measurement.
The accepted definition of a primary method of measurement is given in § 12.1. The essential feature of such a method is that it must operate according to a well-defined measurement equation in which all of the variables can be determined experimentally in terms of SI units. Any limitation in the determination of the experimental variables, or in the theory, must be included within the estimated uncertainty of the method if traceability to the SI is to be established. If a convention is used without an estimate of its uncertainty, true traceability to SI would not be established. In the following section, it is shown that the

Harned cell fulfils the definition of a primary method for the measurement of the acidity function, $p(a_H\gamma_{Cl})$, and subsequently of the pH of buffer solutions.

4 The Harned cell as a Primary Method for the Absolute Measurement of pH

4.1 The Harned cell.
The cell without transference defined by

$$Pt \mid H_2 \mid \text{buffer S, } Cl^- \mid AgCl \mid Ag \qquad \text{Cell I}$$

is known as the Harned cell (7). Chloride ions, in the form of potassium or sodium chloride, are added in order to use the silver-silver chloride electrode . The application of the Nernst equation to the spontaneous cell reaction:

$$\tfrac{1}{2}\, H_2 + AgCl \rightarrow Ag(s) + H^+ + Cl^-$$

yields the potential difference E_I (corrected to 1 atm (101.325 kPa) partial pressure of hydrogen gas,) of the cell as

$$E_I = E^o - [(RT/F) \ln 10] \lg [(m_H\gamma_H/m^o)(m_{Cl}\gamma_{Cl}/m^o)] \qquad (2)$$

which can be rearranged, since $a_H = m_H\gamma_H/m^o$, to give the acidity function

$$p\,(a_H\,\gamma_{Cl}) = -\lg (a_H\,\gamma_{Cl}) = (E_I - E^o)/[(RT/F)\ln 10] + \lg (m_{Cl}/m^o) \qquad (2')$$

where E^o is the standard potential difference of the cell, and hence of the silver-silver chloride electrode, and γ_{Cl} is the activity coefficient of the chloride ion.

Note: The sign of the standard electrode potential of an electrochemical reaction is that displayed on a high impedance voltmeter when the lead attached to standard hydrogen electrode is connected to the minus pole of the voltmeter.

The steps in the use of the cell are summarised in Figure 1 and described in the following paragraphs.

The standard potential difference of the silver/silver chloride electrode, E^o, is determined from a Harned cell in which only HCl is present at a fixed molality (e.g. m = 0.01 mol kg^{-1}). The application of the Nernst equation to the HCl cell

$$Pt \mid H_2 \mid HCl\ (m) \mid AgCl \mid Ag \qquad \text{Cell Ia}$$

gives

$$E_{Ia} = E^o - [(2RT/F) \ln 10] \lg (m_{HCl}/m^o)(\gamma_{\pm HCl}) \qquad (3)$$

where E_{Ia} has been corrected to 1 atmosphere partial pressure of hydrogen gas (101.325 kPa) and $\gamma_{\pm HCl}$ is the mean ionic activity coefficient of HCl.

4.2 Activity coefficient of HCl.

The values of the activity coefficient ($\gamma_{\pm HCl}$) at molality 0.01 mol kg^{-1} and various temperatures are given by Bates and Robinson (8). The standard potential difference depends in some not entirely understood way on the method of preparation of the electrodes, but individual determinations of the activity coefficient of HCl at 0.01 mol kg^{-1} are more uniform than values of E^o. Hence the practical determination of the potential difference of the cell with HCl at 0.01 mol kg^{-1} is recommended at 298.15 K at which the mean ionic activity coefficient is 0.904. Dickson (9) concluded that it is not necessary to repeat the measurement of E^o at other temperatures, but that it is satisfactory to correct published smoothed values by the observed difference in E^0 at 298.15 K.

4.3 The acidity function.

In NMIs measurements of Cells I and Ia are often done simultaneously in a thermostat bath. Subtracting eqn.(3) from (2) gives

$$\Delta E = E_{\mathrm{I}} - E_{\mathrm{Ia}} = -[(RT/F)\ln 10][\lg (m_{\mathrm{H}}\gamma_{\mathrm{H}}/m^o)(m_{\mathrm{Cl}}\gamma_{\mathrm{Cl}}/m^o) - \lg (m_{\mathrm{HCl}}/m^o)^2\gamma^2_{\pm\mathrm{HCl}}] \qquad (4)$$

which is independent of the standard potential difference. Therefore, the subsequently calculated pH does not depend on the standard potential difference and hence does not depend on the assumption that the standard potential of the hydrogen electrode, $E^o_{(\mathrm{H+|\,H2})} = 0$ at all temperatures. Therefore, the Harned cell can give an exact comparison between hydrogen ion activities at two different temperatures (in contrast to statements found elsewhere, see for example (5)).

The quantity $p(a_H\gamma_{Cl}) = -\lg (a_H\gamma_{Cl})$, on the left hand side of (2'), is called the acidity function (5). To obtain the quantity pH (according to eqn. (1)), from the acidity function, it is necessary to evaluate lg γ_{Cl} by independent means. This is done in two steps: (i) the value of lg $(a_H\gamma_{Cl})$ at zero chloride molality, lg $(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})^o$, is evaluated and (ii) a value for the activity of the chloride ion γ^o_{Cl}, at zero chloride molality (sometimes referred to as the limiting or 'trace' activity coefficient (9)) is calculated using the Bates-Guggenheim convention (10). These two steps are described in the following paragraphs.

4.4 Extrapolation of acidity function to zero chloride molality.

The value of lg $(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})^o$ corresponding to zero chloride molality is determined by linear extrapolation of measurements using Harned cells with at least three added molalities of sodium or potassium chloride.

$$-\lg (a_{\mathrm{H}}\gamma_{\mathrm{Cl}}) = -\lg (a_{\mathrm{H}}\gamma_{Cl})^o + Sm_{Cl} \qquad (5)$$

where S is an empirical, but temperature dependent, constant. The extrapolation is linear, which is expected from Brönsted's observations (11) that specific ion interactions between oppositely charged ions are dominant in mixed strong electrolyte systems at constant molality or ionic strength. However, these acidity function measurements are made on mixtures of weak and strong electrolytes at constant buffer molality but not constant total molality. It can be shown (12), that provided the change in ionic strength on addition of chloride is less than 20%, the extrapolation will be linear without detectable curvature. If the latter, less convenient method, of preparation of constant total molality solutions is used, Bates (5) has reported that, for equimolal phosphate buffer, the two methods extrapolate to the same intercept. In an alternative procedure, often useful for partially aqueous mixed solvents where the above extrapolation appears to be curved, multiple application of the Bates-Guggenheim convention to each solution composition gives identical results within the estimated uncertainty of the two intercepts.

4.5 Bates-Guggenheim convention.

The activity coefficient of chloride (like the activity coefficient of the hydrogen ion) is an immeasurable quantity. However, in solutions of low ionic strength ($I < 0.1$ mol kg^{-1}) it is possible to calculate the activity coefficient of chloride ion using Debye-Hückel theory. This is done by adopting the Bates-

Guggenheim convention, which assumes the trace activity coefficient of the chloride ion γ^{o}_{Cl} is given by the expression (10).

$$\lg \gamma^{o}_{Cl} = - A I^{½} / (1 + Ba I^{½}) \qquad (6)$$

where A is the Debye-Hückel temperature dependent constant (limiting slope), a is the *mean* distance of closest approach of the ions (ion size parameter), Ba is set equal to 1.5 (mol kg^{-1})$^{-½}$ at all temperatures in the range 5-50 °C, and I is the ionic strength of the buffer (which for its evaluation requires knowledge of appropriate acid dissociation constants). Values of A as a function of temperature can be found in Table A6 and of B, which is effectively unaffected by revision of dielectric constant data, in Bates (5). When the numerical value of Ba = 1.5 (i.e without units) is introduced into eqn. (6) it should be written as

$$\lg \gamma^{o}_{Cl} = - AI^{½} /([1 + 1.5 (I/m^{o})^{½}] \qquad (6')$$

The various stages in the assignment of primary standard pH values are combined in eqn. (7), which is derived from eqns. (2'), (5), (6')

$$\mathrm{pH(PS)} = \lim m_{Cl \to 0} \{(E_I - E^{o})/[(RT/F) \ln 10] + \lg (m_{Cl}/m^{o})\} - AI^{½} /([1 + 1.5 (I/m^{o})^{½}] \qquad (7)$$

and the steps are are summarised schematically in Figure 1.

5 Sources of Uncertainty in the Use of the Harned cell

5.1 The potential Primary Method and Uncertainty evaluation.

The presentation of the procedure in § 4 highlights the fact that assumptions based on electrolyte theories (7) are used at three points in the method:

(i) Debye-Hückel theory is the basis of the extrapolation procedure to calculate the value for the standard potential of the silver/silver chloride electrode, even though it is a published value of $\gamma_{\pm HCl}$, at e.g. m = 0.01 mol kg^{-1}, that is recommended (§ 4.2) to facilitate E^{o} determination.

(ii) Specific ion interaction theory is the basis for using a linear extrapolation to zero chloride (but the change in ionic strength produced by addition of chloride should be restricted to no more than 20%).

(iii) Debye-Hückel theory is the basis for the Bates-Guggenheim convention used for the calculation of the trace activity coefficient, $\gamma_{Cl}{}^{o}$.

In the first two cases, the inadequacies of electrolyte theories are sources of uncertainty that limit the extent to which the measured pH is a true representation of lg a_H. In the third case, the use of equation (6) or (7) is a convention since the value for Ba is not directly determinable experimentally. Previous recommendations have not included the uncertainty in Ba explicitly within the calculation of the uncertainty of the measurement.

Since eqn. (2) is derived from the Nernst equation applied to the thermodynamically well-behaved platinum-hydrogen and silver-silver chloride electrodes, it is recommended that, when used to measure $-\lg(a_H\gamma_{Cl})$ in aqueous solutions, the Harned cell *potentially* meets the agreed definition of a primary method for the measurement. The word '*potentially*' has been included to emphasise that the method can only achieve primary status if it is operated with the highest metrological qualities (see § 6.1-6.2). Additionally, if the Bates-Guggenheim convention is used for the calculation of lg γ^{o}_{Cl} , the Harned cell *potentially* meets the agreed definition of a primary method for the measurement of pH subject to this

convention if a realistic estimate of its uncertainty is included. The uncertainty budget for the primary method of measurement by the Harned cell (Cell I) is given in the Annex § 13.

Note: The experimental uncertainty for a typical primary pH(PS) measurement is of the order of 0.004 (see Table 4).

5.2 Evaluation of Uncertainty of Bates-Guggenheim convention.
In order for a measurement of pH made with a Harned cell to be traceable to the SI system, an estimate of the uncertainty of each step must be included in the result. Hence it is recommended that an estimate of the uncertainty of 0.01 (95% confidence interval) in pH associated with the Bates-Guggenheim convention is used. The extent to which the Bates-Guggenheim convention represents the "true" (but immeasurable) activity coefficient of the chloride ion can be calculated by varying the coefficient Ba between 1.0 and 2.0 (mol $kg^{-1})^{-½}$. This corresponds to varying the ion-size parameter between 0.3 and 0.6 nm, yielding a range of ± 0.012 (at I = 0.1 mol kg^{-1}) and ± 0.007 (at I = 0.05 mol kg^{-1}) for γ_{Cl} calculated using equation (7). Hence an uncertainty of 0.01 should cover the full extent of variation. This must be included in the uncertainty of pH values that are to be regarded as traceable to the SI. pH values stated without this contribution to their uncertainty cannot be considered to be traceable to the SI.

5.3 Hydrogen ion concentration.
It is rarely required to calculate hydrogen ion concentration from measured pH. Should such a calculation be required, the only consistent, logical way of doing it is to assume $\gamma_H = \gamma_{Cl}$ and set the latter to the appropriate Bates-Guggenheim conventional value. The uncertainties are then those derived from the Bates-Guggenheim convention.

5.4 Possible future approaches.
Any model of electrolyte solutions which takes into account both electrostatic and specific interactions for individual solutions would be an improvement over use of the Bates-Guggenheim convention. It is hardly reasonable that a fixed value of the ion-size parameter should be appropriate for a diversity of selected buffer solutions. It is hoped that the Pitzer model of electrolytes (13), which uses a virial equation approach, will provide such an improvement, but data in the literature are insufficiently extensive to make these calculations at the present time. From limited work at 25 °C done on phosphate and carbonate buffers, it seems that changes to Bates-Guggenheim recommended values will be small (14). It is possible that some anomalies attributed to liquid junction potentials may be resolved.

6 Primary Buffer Solutions and Required Properties

6.1 Requisites for highest metrological quality.
In the previous sections, it has been shown that the Harned cell provides a primary method for the determination of pH. In order for a particular buffer solution to be considered a primary buffer solution, it must be of the "highest metrological" quality (15) in accordance with the definition of a primary standard. It is recommended that it have the following attributes (16, 17; 5, p.95):

1. High buffer value in the range 0.016 – 0.07 (mol OH^-)/pH.
2. Small dilution value at half concentration (change in pH with change in buffer concentration) in the range 0.01 – 0.20.
3. Small dependence of pH on temperature in the range 0.001 – 0.01 K^{-1}.
4. Low residual liquid junction potential < 0.01 in pH (see § 7).
5. Ionic strength ≤ 0.1 mol kg^{-1} to permit applicability of Bates-Guggenheim convention.

6. NMI certificate for specific batch.
7. Reproducible purity of preparation (lot to lot differences of ΔpH(PS) < 0.003).
8. Long term stability of stored solid material.

Values for the above and other important parameters for the selected primary buffer materials (see § 6.2) are given in Table 1.

Note: The long-term stability of the solid compounds (>5 years) is a requirement not met by borax (16). There are also doubts about the extent of polyborate formation in 0.05 mol kg^{-1} borax solutions and hence this solution is not accorded primary status.

6.2 Primary standard buffers.

Since there can be significant variations in the purity of samples of a buffer of the same nominal chemical composition, it is essential that the primary buffer material used has been certified with values that have been measured with Cell I. The Harned cell has been used by many NMIs for accurate measurements of the pH of buffer solutions. Comparisons of such measurements have been carried out under EUROMET collaboration(18), which have demonstrated the high comparability of measurements (0.005 in pH) in different laboratories of samples from the same batch of buffer material. Typical values of the pH(PS) of the 7 solutions from the 6 accepted primary standard reference buffers, which meet the conditions stated in § 6.1, are listed in Table 2. These listed pH(PS) values have been derived from certificates issued by NBS/NIST over the past 35 years. Batch-to-batch variations in purity can result in changes in the pH value of samples of at least 0.003. The typical values in Table 2 should not be used in place of the certified value (from a Harned cell measurement) for a specific batch of buffer material.

The required attributes listed in § 6.1 effectively limit the range of primary buffers available to between pH 3 and 10 (at 25 ^{o}C). Calcium hydroxide and potassium tetraoxalate have been excluded because the contribution of hydroxyl or hydrogen ions to the ionic strength is significant. Also excluded are the nitrogen bases of the type BH^{+} (such as tris-hydroxymethyl aminomethane and piperazine phosphate) and the zwitterionic buffers (e.g. HEPES and MOPS (19)). These do not comply because either the Bates-Guggenheim convention is not applicable, or the liquid junction potentials are high. This means the choice of primary standards is restricted to buffers derived from oxy-carbon, -phosphorus, -boron and mono, di- and tri-protic carboxylic acids. In the future, other buffer systems may fulfil the requirements listed in § 6.1.

7 Consistency of Primary Buffer Solutions

7.1 Consistency and the liquid junction potential

Primary methods of measurement are made with cells without transference as described in § 1-6 (Cell I). Less complex, secondary methods use cells with transference, which contain liquid junctions. A single liquid junction potential is immeasurable, but differences in liquid junction potential can be estimated. Liquid junction potentials vary with the composition of the solutions forming the junction and the geometry of the junction.

Eqn. (2) for Cell I applied successively to two primary standard buffers, PS_1, PS_2, gives

$$\Delta pH_I = pH_I(PS_2) - pH_I(PS_1) = \lim m_{Cl \to 0} \{ E_I(PS_2)/k - E_I(PS_1)/k\} - A\{I_{(2)}^{1/2}/([1 + 1.5\ (I_{(2)}/m^{o})^{1/2}] - I_{(1)}^{1/2}/([1 + 1.5\ (I_{(1)}/m^{o})^{1/2}]\} \quad (8)$$

where the last term is the ratio of trace chloride activity coefficients $\lg[\gamma^{\rho}_{Cl(2)}/\gamma^{\rho}_{Cl(1)}]$, conventionally evaluated *via* B-G eqn (6').

Note 1: Since the convention may unevenly affect the $\gamma^{\rho}_{Cl(2)}$ and $\gamma^{\rho}_{Cl(1)}$ estimations, ΔpH_I differs from the true value by the unknown $\{\lg[\gamma^{\rho}_{Cl(2)}/\gamma^{\rho}_{Cl(1)}] - A[I_{(1)}^{½}/(1+1.5I_{(1)}^{½}) - I_{(2)}^{½}/(1+1.5I_{(2)}^{½})]\}$ contribution.
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A second method of comparison is by measurement of Cell II in which there is a salt bridge with two free diffusion liquid junctions

$$Pt \mid H_2 \mid PS_2 \mid KCl\ (\geq 3.5 mol\ dm^{-3}) \mid PS_1 \mid H_2 \mid Pt \qquad \text{Cell II}$$

for which the spontaneous cell reaction is a dilution,

$$H^+(PS_1) \rightarrow H^+(PS_2)$$

gives the pH difference from Cell II as

$$\Delta pH_{II} = pH_{II}(PS_2) - pH_{II}(PS_1) = E_{II}/k - [(E_{j2} - E_{j1})/k] \qquad (9)$$

where the subscript II is used to indicate that the pH difference between the same two buffer solutions is now obtained from Cell II. ΔpH_{II} differs from ΔpH_I (and both differ from the true value ΔpH_I) since it depends on unknown quantity, the residual liquid junction potential, RLJP = (E_{j2} - E_{j1}), whose exact value could be determined if the true ΔpH were known.

Note 2: The subject of liquid junction effects in ion-selective electrode potentiometry has been comprehensively reviewed (20). Harper (21) and Bagg (22) have made computer calculations of liquid junction potentials for simple three ion junctions (such as HCl + KCl) the only ones for which mobility and activity coefficient data are available. Breer, Ratkje and Olsen (23) have thoroughly examined the possible errors arising from the commonly made approximations in calculating liquid junction potentials for three-ion junctions. They concluded that the assumption of linear concentration profiles has less severe consequences (~ 0.1 – 1.0 mV) than the other two assumptions of the Henderson treatment, namely constant mobilities and neglect of activity coefficients, which can lead to errors of ~10 mV. Breer *et al*. concluded that their calculations supported an earlier statement (24) that in ion-selective electrode potentiometry, the theoretical Nernst slope, even for dilute sample solutions, could never be attained because of liquid junction effects.

Note 3: According to IUPAC recommendations on nomenclature and symbols (3), a single vertical bar (|) is used to represent a phase boundary, a dashed vertical bar (¦) represents a liquid-liquid junction between two electrolyte solutions (across which a potential difference will occur), and a double dashed vertical bar (¦¦) represents a similar liquid junction, in which the liquid junction potential is assumed to be effectively zero (~1% of cell potential). Hence, the term in square brackets on the right hand side of eqn, (9) is usually ignored and the liquid junction represented by ¦¦ . In the Annex, the symbol ¦ is used because the error associated with the liquid junction is included in the analysis.

Note 4: The polarity of Cell II will be negative on the left, i.e. – | +, when $pH(PS_2) > pH(PS_1)$. The liquid junction potential E_j of a single liquid junction is defined as the difference of the potential of the solution of interest, e.g. a buffer solution, minus the potential of the KCl solution, for instance in Cell II, $E_{j1} = E(S_1) - E(KCl)$ and $E_{j2} = E(S_2) - E(KCl)$. It is negative when the solution of interest is an acid solution and positive when it is an alkaline solution, provided E_j is principally caused by the hydrogen, or hydroxyl, ion content of the solution of interest (and only to a smaller degree by its alkali ions or anions). The residual liquid junction potential, the difference $E_j(right) - E_j(left)$, depends on the relative magnitudes of the individual E_j values and

has the opposite polarity to the potential difference E of the cell. Hence, in Cell II the residual liquid junction potential, $E_{j1}(PS_1) - E_{j2}(PS_2)$, has a polarity $+|-$ when $pH(S_2) > pH(S_1)$.

Notwithstanding the foregoing, comparison of pH_{II} values from the Cell II with two liquid junctions (eqn. 9) with the assigned pH_I (PS) values for the same two primary buffers measured with Cell I (eqn. 8) makes an estimation of residual liquid junction potentials (RLJP) possible (5):

$$[pH_I(PS_2) - pH_{II}(PS_2)] - [(pH_I(PS_1) - pH_{II}(PS_1)] = (E_{j2} - E_{j1})/k = \text{RLJP} \qquad (10)$$

With the value of RLJP set equal to zero for equimolal phosphate buffer (taken as PS_1) then $[pH_I(PS_2) - pH_{II}(PS_2)]$ is plotted against pH(PS). Results for free diffusion liquid junctions formed in a capillary tube with cylindrical symmetry at 25 °C are shown in Figure 2 (25, and references cited therein).

Note 5: For 0.05 mol kg^{-1} tetraoxalate, the published values (26) for Cell II with free diffusion junctions are wrong (27, 28).

Values such as those shown in Figure 2 give an indication of the extent of possible systematic uncertainties for primary standard buffers arising from three sources:

(i) experimental uncertainties, including any variations in the chemical purity of primary buffer materials (or variations in the preparation of the solutions) if measurements of Cells I and II were not made in the same laboratory at the same occasion.

(ii) variation in residual liquid junction potentials between primary buffers.

(iii) inconsistencies resulting from the application of the Bates-Guggenheim convention to chemically different buffer solutions of ionic strengths less than 0.1 mol kg^{-1}.

It may be concluded from examination of the results in Figure 2, that a consistency no better than 0.01 can be ascribed to the primary pH standard solutions of Table 2 in the range 3-10 pH. This value will be greater for less reproducibly formed liquid junctions than the free diffusion type with cylindrical symmetry.

Note 6: Considering the conventional nature of eqn.(10), and that the irreproducibility of formation of geometry-dependent devices exceeds possible bias between carefully formed junctions of known geometry, the RLJP contribution, which is included in the difference between measured potential differences of cells with transference, is treated as a statistical, and not a systematic error.

Note 7: Values of RLJP depend on the Bates-Guggenheim convention through the last term in eqn. (8) and would be different if another convention were chosen. This interdependence of the single ion activity coefficient and the liquid junction potential may be emphasised by noting that it would be possible *arbitrarily* to reduce RLJP values to zero for each buffer by adjusting the ion-size parameter in eqn. (6).

7.2 Computational approach to consistency.

The consistency between conventionally assigned pH values can also be assessed by a computational approach. The pH values of standard buffer solutions have been calculated from literature values of acid dissociation constants by an iterative process. The arbitrary extension of Bates-Guggenheim convention for chloride ion, to all ions, leads to the calculation of ionic activity coefficients of all ionic species, ionic strength, buffer capacity and calculated pH values. The consistency of these values with primary pH values obtained using Cell I was 0.01 or lower between 10 and 40 °C (29, 30).

8 Secondary Standards and Secondary Methods of Measurement

8.1 Secondary standards derived from Harned cell Measurements.
Substances that do not fulfil all the criteria for primary standards but to which pH values can be assigned using Cell I are considered to be secondary standards. Reasons for their exclusion as primary standards include, *inter alia*:

(i) Difficulties in achieving consistent, suitable chemical quality (e.g. ethanoic acid is a liquid).
(ii) High liquid junction potential, or inappropriateness of the Bates-Guggenheim convention (e.g. other charge-type buffers)

Therefore, they do not comply with the stringent criterion for a primary measurement of being of the highest metrological quality. Nevertheless, their pH(SS) values can be determined. Their consistency with the primary standards should be checked with the method described in § 7. The primary and secondary standard materials should be accompanied by certificates from NMIs in order for them to be described as certified reference materials (CRMs). Some illustrative pH(SS) values for secondary standard materials (5, 17, 25, 31, 32) are given in Table 3.

8.2 Secondary standards derived from primary standards.
In most applications, the use of a high-accuracy primary standard for pH measurements is not justified, if a traceable secondary standard of sufficient accuracy is available. Several designs of cells are available for comparing the pH values of two buffer solutions. However, there is no primary method for measuring the *difference* in pH between two buffer solutions for reasons given in § 8.6. Such measurements could involve either using a cell successively with two buffers, or a single measurement with a cell containing two buffer solutions separated by one or two liquid junctions.

8.3 Secondary standards derived from primary standards of the same nominal composition using cells without salt bridge.
The most direct way of comparing pH(PS) and pH(SS) is by means of the single junction Cell III (33).

$Pt|H_2|$Buffer S_2 ¦ ¦ Buffer $S_1|H_2|Pt$ Cell III

The cell reaction for the spontaneous dilution reaction is the same as for Cell II and the pH difference is given by

$$pH(S_2) - pH(S_1) = E_{III}/k \qquad (11)$$

The buffer solutions containing identical $Pt|H_2$ electrodes with an identical hydrogen pressure are in direct contact via a vertical sintered glass disk of a suitable porosity (40 μm). The liquid junction potential formed between the two standards of nominally the same composition will be particularly small and is estimated to be in the μV range. It will therefore be less than 10% of the potential difference measured if the pH(S) values of the standard solutions are in the range $3 \le pH(S) \le 11$ and the difference in their pH(S) values is not larger than 0.02. Under these conditions, the liquid junction potential is not dominated by the hydrogen and hydroxyl ions but by the other ions (anions, alkali metal ions). The proper functioning of the cell can be checked by measuring the potential difference when both sides of the cell contain the same solution.

8.4 Secondary standards derived from primary standards using cells with salt bridge.
The cell that includes a hydrogen electrode (corrected to 1 atm. (101.325 kPa) partial pressure of hydrogen) and a reference electrode, the filling solution of which is a saturated or high concentration of

the almost equitransferent electrolyte, potassium chloride, hence minimising the liquid junction potential, is:

$$\text{Ag} \mid \text{AgCl} \mid \text{KCl}\ (\geq 3.5 \text{mol dm}^{-3}) \,\vdots\, \text{buffer S} \mid \text{H}_2 \mid \text{Pt} \qquad \text{Cell IV}$$

Note 1: Other electrolytes, e.g. rubidium or cesium chloride, are more equitransferent (34).

Note 2: Cell IV is written in the direction: *reference* | *indicator*
(i) for conformity of treatment of all hydrogen ion-responsive electrodes and ion-selective electrodes with various choices of reference electrode, and partly,
(ii) for the practical reason that pH meters usually have one low impedance socket for the reference electrode, assumed negative, and a high impedance terminal with a different plug, usually for a glass electrode.
With this convention, whatever the form of hydrogen ion-responsive electrode used (e.g. glass or quinhydrone), or whatever the reference electrode, the potential of the hydrogen-ion responsive electrode always decreases (becomes more negative) with increasing pH (see Figure 3).
This convention was used in the 1985 document (2) and is also consistent with the treatment of ion-selective electrodes (35). In effect, it focuses attention on the indicator electrode, for which the potential is then given by the Nernst equation for the single electrode potential, written as a reduction process, in accord with the Stockholm convention (36):

For $\text{Ox} + n\text{e}^- \rightarrow \text{Red}$, $\qquad E = E^{\text{o}} - (k/n) \lg [a_{\text{red}}]/[a_{\text{ox}}]$

(where a is activity), or, for the hydrogen gas electrode at 1 atm. partial pressure of hydrogen gas:

$\text{H}^+ + \text{e}^- \rightarrow \tfrac{1}{2}\,\text{H}_2$ $\qquad E = E^{\text{o}} + k \lg a_{\text{H+}} = E^{\text{o}} - k\text{pH}$

The equation for Cell IV is therefore:

$$\text{pH(S)} = -[E_{\text{IV}}(\text{S}) - E_{\text{IV}}{}^{\text{o}'} + E_{\text{j}}]/k \qquad (12)$$

in which $E_{\text{IV}}{}^{\text{o}'}$ is the standard potential, which includes the term $\lg a_{\text{Cl}}/m^{\text{o}}$, and E_{j} is the liquid junction potential.
Note 3: Mercury- mercury(I) chloride (calomel) and thallium amalgam-thallium (I) chloride reference electrodes are alternative choices to the silver-silver chloride electrode in Cell IV.

The consecutive use of two such cells containing buffers S_1 and S_2 gives the pH difference of the solutions

$$\text{pH}(S_2) - \text{pH}(S_1) = -[E_{\text{IV}}(S_2) - E_{\text{IV}}(S_1)]/k - [E_{\text{j2}} - E_{\text{j1}}]/k \qquad (13)$$

in which the second term is the residual liquid junction potential (RLJP), (see § 7.1).

Note 4: Experimentally, a three-limb electrode vessel allowing simultaneous measurement of two Cell II may be used (25) with the advantage that the stability with time of the electrodes and of the liquid junctions can be checked. The measurement of cells of type II, which has a salt bridge with two liquid junctions, has been discussed in § 7.

Cells II and IV may also be used to measure the value of secondary buffer standards that are not compatible with the silver/silver chloride electrode used in Cell I. Since the liquid junction potentials in Cells II and IV are minimised by the use of an equitransferent salt, these cells are suitable for use with secondary buffers that have a different concentration and/or an ionic strength greater than the limit ($I \leq 0.1$ mol kg^{-1}) imposed by the Bates-Guggenheim convention. They may, however, also be used for comparing solutions of the same nominal composition.

8.5 Secondary standards from glass electrode cells.

Measurements cannot be made with a hydrogen electrode in Cell IV, for example, if the buffer is reduced by hydrogen gas at the platinum (or palladium-coated platinum) electrode. Cell V involving a glass electrode and silver-silver chloride reference electrode may be used instead in consecutive measurements, with two buffers PS_2, SS_2 (see §11.3 for details).

8.6 Secondary methods.
The equations given for Cells II to V show that these cannot be considered primary (ratio) methods for measuring pH difference (1), (see also § 12.1) because the cell reactions involve transference, or the irreversible inter-diffusion of ions, and hence a liquid junction potential contribution to the measured potential difference. The value of this potential difference depends on the ion constituents, their concentrations and the geometry of the liquid junction between the solutions. Hence, the measurement equations contain terms that, although small, are not quantifiable and the methods are secondary not primary.

9 Consistency of Secondary Standard Buffer Solutions established with respect to Primary Standards.

9. 1 Summary of procedures for establishing secondary standards.
The following procedures may be distinguished for establishing secondary standards (SS) with respect to primary standards:
(i) For SS of the same nominal composition as PS use Cell III or Cell II
(ii) For SS of different composition use Cell IV or Cell II
(iii) For SS not compatible with platinum hydrogen electrode use Cell V (see § 11.1).
Although any of Cells II to V could be used for certification of secondary standards with stated uncertainty, employing different procedures would lead to inconsistencies. It would be difficult to define specific terminology to distinguish each of these procedures or to define any rigorous hierarchy for them. Hence, the methods should include estimates of the typical uncertainty for each. The choice between methods should be made according to the uncertainty required for the application (see § 10 and Table 4).

9.2 Secondary standard evaluation from primary standards of same composition.
It is strongly recommended that the preferred method for assigning secondary standards should be procedure (i) in which measurements are made with respect to the primary buffer of nominally the same chemical composition. All secondary standards should be accompanied by a certificate relating to that particular batch of reference material as significant batch to batch variations are likely to occur. Some secondary standards are disseminated in solution form. The uncertainty of the pH values of such solutions may be larger than those for material disseminated in solid form.

9.3 Secondary standard evaluation when there is no primary standard of the same composition.
It may sometimes be necessary to set up a secondary standard when there is no primary standard of the same chemical composition available. It will therefore be necessary to use either Cell II, IV or V, and a primary or secondary standard buffer of different chemical composition. Buffers measured in this way will have a different status from those measured with respect to primary standards because they are not directly traceable to a primary standard of the same chemical composition. This different status should be reflected in the, usually larger, uncertainty quoted for such a buffer. Since this situation will only occur for buffers when a primary standard is not available, no special nomenclature is recommended to distinguish the different routes to secondary standards. Secondary buffers of a composition different from those of primary standards can also be derived from measurements on Cell I, provided the buffer is

compatible with Cell I. However, the uncertainty of such standards should reflect the limitations of the secondary standard (see Table 4).

10. Target Uncertainties for the Measurement of Secondary Buffer Solutions.

10.1 Uncertainties of secondary standards derived from primary standards.
Cells II to IV (and occasionally Cell V) are used to measure secondary standards with respect to primary standards. In each case, the limitations associated with the measurement method will result in a greater uncertainty for the secondary standard than the primary standard from which it was derived.
Target uncertainties are listed in Table 4. However, these uncertainties do not take into account the uncertainty contribution arising from the adoption of the Bates-Guggenheim convention to achieve traceability to SI units.

10.2 Uncertainty evaluation (37).
Summaries of typical uncertainty calculations for Cells I - V are given in the Annex (§ 13).

11. Calibration of pH Meter-Electrode Assemblies and Target Uncertainties for Unknowns.

11.1 Glass electrode cells.
Practical pH measurements are carried out by means of Cell V

reference electrode | KCl ($c \geq 3.5$mol dm^{-3}) ¦¦ solution(pH(S) or pH(X)) | glass electrode (V)

These cells often use glass electrodes in the form of single probes or combination electrodes (glass and reference electrodes fashioned into a single probe, a so-called 'combination electrode').

The potential difference, E_V, expressed in terms of the potentials of the glass and reference electrodes, E_{glass} and E_{ref} , and the liquid junction potential, E_j, (see § 7), is given by

$$E_V = E_{glass} - E_{ref} + E_j \qquad (14)$$

Various random and systematic effects must be noted when using these cells for pH measurements:
(i) Glass electrodes may exhibit a slope of the E vs. pH function smaller than the theoretical value [$k = (RT/F)\ln 10$], often called a sub-Nernstian response or practical slope k', which is experimentally determinable. A theoretical explanation for the sub-Nernstian response of pH glass electrodes in terms of the dissociation of functional groups at the glass surface has been given (38).
(ii) The response of the glass electrode may vary with time, history of use, and memory effects. It is recommended that the response time and the drift of the electrodes be taken into account (39).
(iii) E_{glass} is strongly temperature dependent as to a lesser extent are E_{ref} and E_j. Calibrations and measurements, should therefore be carried out under temperature controlled conditions.
(iv) Liquid junction potentials, E_j, vary with the composition of the solutions forming the junction, e.g. with pH (see Figure 2). Hence they will differ if one solution (pH(S) or pH(X)) in Cell(V) is replaced by another. They are also affected by the geometry of the liquid junction device. Hence they may be different if a free-diffusion type junction, such as that used to measure the RLJP (see § 7), is replaced by another type, such as a sleeve, ceramic diaphragm, fibre or platinum junction (39, 40).

(v) Liquid junction devices, particularly some commercial designs, may suffer from memory and clogging effects.
(vi) E_j may be subject to hydrodynamic effects e.g. stirring.

Since these effects introduce errors of unknown magnitude, the measurement of an unknown sample requires a suitable calibration procedure. Three procedures are in common use based on calibrations at one point (one point calibration), two points (two-point calibration or bracketing) and a series of points (multi-point calibration).

11.2 Target uncertainties for unknowns.
Uncertainties in pH(X) are obtained, as shown below, by several procedures involving different numbers of experiments. Numerical values of these uncertainties obtained from the different calibration procedures are therefore not directly comparable. It is therefore not possible at the present time to make a universal recommendation of the best procedure to adopt for all applications. Hence, the target uncertainty for the unknown is given which the operator of a pH meter electrode assembly may reasonably seek to achieve. Values are given for each of the three techniques (see Table 4) but the uncertainties attainable experimentally are critically dependent on the factors listed in § 11.1 above, on the quality of the electrodes and on the experimental technique for changing solutions.

In order to obtain the overall uncertainty of the measurement, uncertainties of the respective pH(PS) or pH(SS) values must be taken into account (see Table 4). Target uncertainties given below, and in Table 4, refer to calibrations performed by the use of standard buffer solutions with an uncertainty U(pH(PS)) or U(pH(SS)) 0.01. The overall uncertainty becomes higher if standards with higher uncertainties are used.

11.3 One-point calibration
A single point calibration is insufficient to determine both slope and (one) point parameters. The theoretical value for the slope can be assumed but the practical slope may be up to 5% lower. Alternatively, a value for the practical slope can be assumed from the manufacturer's prior calibration. The one-point calibration therefore yields only an estimate of pH(X). Since both parameters may change with age of the electrodes, this is not a reliable procedure. Based on a measurement for which ΔpH = |pH(X) - pH(S)| = 5, the expanded uncertainty would be U = 0.5 in pH(X) for k' = 0.95k, but assumed theoretical, or U= 0.3 in pH(X) for ΔpH = |pH(X) –pH(S)| = 3 (see Table 4). This approach could be satisfactory for certain applications. The uncertainty will decrease with decreasing difference pH(X) – pH(S) and be smaller if k' is known from prior calibration.

11.4 Two-point calibration [target uncertainty, U(pH(X)) = 0.02 - 0.03 at 25 °C]
In the majority of practical applications, glass electrodes cells (Cell V) are calibrated by two-point calibration, or bracketing, procedure using two standard buffer solutions, with pH values pH(S_1) and pH(S_2), bracketing the unknown pH(X). Bracketing is often taken to mean that the pH(S_1) and pH(S_2) buffers selected should be those that are immediately above and below pH(X). This may not be appropriate in all situations and choice of a wider range may be better.

If the respective potential differences measured are E_V (S_1), E_V (S_2) and E_V (X), the pH value of the unknown, pH(X), is obtained from eqn.(15)

$$pH(X) = pH(S_1) - [E_V(X) - E_V(S_1)]/k' \qquad (15)$$

where the practical slope factor (k') is given by

$$k' = [E_V(S_1) - E_V(S_2)]/[pH(S_2) - pH(S_1)] \quad (16)$$

An example is given in the Annex § 13.

11.5 Multi-point calibration [target uncertainty: $U(pH(X))= 0.01 - 0.03$ at 25 °C].
Multi-point calibration is carried out using up to five standard buffers (39, 40). The use of more than five points does not yield any significant improvement in the statistical information obtainable.

The calibration function of cell (V) is given by eqn.(17)

$$E_V(S) = E_V^{o} - k' pH(S) \quad (17)$$

where $E_V(S)$ is the measured potential difference when the solution of pH(S) in Cell V is a primary or secondary standard buffer. The intercept, or 'standard potential', $E_V°$ and k', the practical slope are determined by linear regression of eqn. (17) (39- 41).

pH(X) of an unknown solution is then obtained from the potential difference, $E_V(X)$, by

$$pH(X) = [E_V^{o} - E_V(X)]/k' \quad (18)$$

Additional quantities obtainable from the regression procedure applied to eqn. (17) are the uncertainties $u(k')$ and $u(E_V^{o})$ (40). Multi-point calibration is recommended when minimum uncertainty and maximum consistency are required over a wide range of pH(X) values. This applies, however, only to that range of pH values in which the calibration function is truly linear. In non-linear regions of the calibration function, the two-point method has clear advantages provided that $pH(S_1)$ and $pH(S_2)$ are selected to be as close to pH(X) as possible..

Details of the uncertainty computations for the multi-point calibration have been given (40) and an example is given in the Annex. The uncertainties are recommended as a means of checking the performance characteristics of pH meter-electrode assemblies (40). By careful selection of electrodes for multi-point calibration, uncertainties of the unknown pH(X) can be kept as low as $U(pH(X)) = 0.01$.

In modern microprocessor pH meters, potential differences are often transformed automatically into pH values. Details of the calculations involved in such transformations, including the uncertainties, are available (41).

12 GLOSSARY (2, 15, 44)

12.1 Primary Method of Measurement
A primary method of measurement is a method having the highest metrological qualities, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units.
A primary direct method measures the value of an unknown without reference to a standard of the same quantity.
A primary ratio method measures the value of a ratio of an unknown to a standard of the same quantity; its operation must be completely described by a measurement equation.

12.2 Primary standard

Standard that is designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to other standards of the same quantity.

12.3 Secondary standard
Standard whose value is assigned by comparison with a primary standard of the same quantity.

12.4 Traceability
Property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties. The concept is often expressed by the adjective traceable. The unbroken chain of comparisons is called a traceability chain.

12.5 Primary pH Standards.
Aqueous solutions of selected reference buffer solutions to which pH(PS) values have been assigned over the temperature range 0 – 50 °C from measurements on cells without transference, called Harned cells, by use of the Bates-Guggenheim Convention.

12.6 Bates-Guggenheim Convention
A convention based on a form of the Debye-Hückel equation which approximates the logarithm of the single ion activity coefficient of chloride and uses a fixed value of 1.5 for the product *Ba* in the denominator at all temperatures in the range 0-50 ^{o}C (see eqns. (4), (5)) and ionic strength of the buffer < 0.1 mol kg^{-1}.

12.7 Secondary pH Standards
Values may be assigned to secondary standard pH(SS) solutions at each temperature:
(i) with reference to [pH(PS)] values of a primary standard of the same nominal composition by Cell III.
(ii) with reference to [pH(PS)] values of a primary standard of different composition by Cells II, IV or V.
(iii) by use of Cell I.
Note: This is an exception to the usual definition, see § 12.3).

12.8 pH glass electrode.
Hydrogen-ion responsive electrode usually consisting of a bulb, or other suitable form, of special glass attached to a stem of high resistance glass complete with internal reference electrode and internal filling solution system. Other geometrical forms may be appropriate for special applications e.g. capillary electrode for measurement of blood pH.

12.9 Glass electrode error
Deviation of a glass electrode from the hydrogen-ion response function. An example often encountered is the error due to sodium ions at alkaline pH values, which by convention is regarded as positive.

12.10 Hydrogen gas electrode.
A thin foil of platinum electrolytically coated with a finely divided deposit of platinum or (in the case of a reducible substance) palladium metal, which catalyses the electrode reaction: $H^{+} + e \rightarrow \frac{1}{2}H_2$ in solutions saturated with hydrogen gas. It is customary to correct measured values to standard 1 atm (101.325 kPa) partial pressure of hydrogen gas.

12.11 Reference electrode.

External electrode system which comprises an inner element, usually silver-silver chloride, mercury-mercury(I) chloride (calomel) or thallium amalgam-thallium(I) chloride, a chamber containing the appropriate filling solution (see 12.14) and a device for forming a liquid junction, e.g. capillary, ceramic plug, frit or ground glass sleeve.

12.12 Liquid junction.
Any junction between two electrolyte solutions of different composition. Across such a junction there arises a potential difference, called the liquid junction potential. In cells II, IV, V, the junction is between the pH standard or unknown solution and the filling solution, or the bridge solution, (q.v.) of the reference electrode.

12.13 Residual liquid junction potential (RLJP) error.
Error arising from breakdown in the assumption that the liquid junction potentials cancel in cell II when solution X is substituted for solution S in the Cell V.

12.14 Filling solution (of a reference electrode)
Solution containing the anion to which the reference electrode of cells IV and V is reversible, e.g. chloride for silver-silver chloride electrode. In the absence of a bridge solution (*q.v.*), a high concentration of filling solution comprising almost equitransferent cations and anions is employed as a means of maintaining the liquid junction potential small and approximately constant on substitution of unknown solution for standard solution(s),

12.15 Bridge (or salt bridge) solution (of a double junction reference electrode)
Solution of high concentration of inert salt, preferably comprising cations and anions of equal mobility, optionally interposed between the reference electrode filling and both the unknown and standard solution, when the test solution and filling solution are chemically incompatible. This procedure introduces into the cell a second liquid junction formed, usually, in a similar way to the first.

12.16 Calibration
Set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument, or measuring system, or values represented by a material measure or a reference material, and the corresponding values realised by standards.

12.17 Uncertainty (of a measurement)
Parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand.

12.18 Standard uncertainty, u_x
Uncertainty of the result of a measurement expressed as a standard deviation.

12.19 Combined standard uncertainty, $u_c(y)$
Standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances, or covariances of these other quantities, weighted according to how the measurement result varies with changes in these quantities.

12.20 Expanded uncertainty, U.
Quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand.

Note 1. The fraction may be viewed as the coverage probability or level of confidence of the interval.
Note 2. To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterised by the measurement result and its combined standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.
Note 3. Expanded uncertainty is sometimes termed overall uncertainty.

12.22 Coverage factor (k)
Numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty
Note: A coverage factor, k, is typically in the range 2 to 3. The value 2 is used throughout in the Annex.

13. ANNEX- Measurement uncertainty

Examples are given of uncertainty budgets for pH measurements at the primary, secondary and working level. The calculations are done in accordance with published procedures (15, 37).
When a measurement (y) results from the values of a number of other quantities, $y = f(x_1, x_2, \ldots x_I)$, the combined standard uncertainty of the measurement is obtained from the square root of the expression

$$u_c^2(y) = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i) \qquad \text{(A1)}$$

where $\frac{\partial f}{\partial x_i}$ is called the sensitivity coefficient (c_i).
The uncertainty stated is the expanded uncertainty, U, obtained by multiplying the standard uncertainty, $u_c(y)$, by an appropriate coverage factor k . When the result has a large number of degrees of freedom, the use of a value for $k = 2$ leads to approximately 95% confidence that the true value lies in the range $\pm U$.
The following sections give illustrative examples of the uncertainty calculations for Cells I – V.
After the assessment of uncertainties, there should be a reappraisal of experimental design factors and statistical treatment of the data, with due regard for economic factors before the adoption of more elaborate procedures.

A1 Uncertainty budget for the primary method of measurement using Cell I.
Experimental details have been published (42-45).

A 1.1 Measurement Equations
The primary method for the determination of pH(PS) values consists of the following steps (§ 4.1):

1. Determination of the standard potential of the Ag|AgCl electrode from the acid-filled cell (Cell Ia)

$$E^\circ = E_a + 2k \lg (m_{HCl}/m^\circ) + 2k \lg \gamma_{HCl} + (k/2) \lg (p^\circ/p) \qquad \text{(A2) cf. (3)}$$

where $E_{Ia} = E_a + (k/2) \lg (p^\circ/p)$, $k = RT/F$ ln 10 and p is the partial pressure of hydrogen in Cell Ia and p° the standard pressure.

2. Determination of the acidity function, $p(a_H\gamma_{Cl})$, in buffer-filled cell (Cell I)

$$- \lg(a_H\gamma_{Cl}) = (E_b - E^\circ)/k + \lg (m_{Cl}/m^\circ) + (1/2) \lg (p^\circ/p) \qquad \text{(A3) cf. (2)}$$

where $E_I = E_b + (k/2) \lg (p^\circ/p)$

and p is the partial pressure of hydrogen in Cell I and p^o the standard pressure.

3. Extrapolation of the acidity function to zero chloride concentration

$$-\lg(a_H\gamma_{Cl}) = -\lg(a_H\gamma_{Cl})^o + Sm_{Cl} \qquad \text{(A4) cf. (5)}$$

4. pH Determination

$$pH(PS) = -\lg(a_H\gamma_{Cl})^o + \lg\gamma_{Cl}^{\,o} \qquad \text{(A5)}$$

where $\lg\gamma_{Cl}^{\,o}$ is calculated from the Bates-Guggenheim convention (see eqn. 6). Values of the Debye-Hückel limiting law slope for 0 to 50 ºC are given in Table A6 (46).

A 1.2 Uncertainty Budget
Example: PS = 0.025 mol kg^{-1} disodium hydrogen phosphate + 0.025 mol kg^{-1} potassium dihydrogen phosphate.

Table A1a. Calculation of standard uncertainty of the standard potential of the silver-silver chloride electrode (E^o) from measurements in m_{HCl} = 0.01 mol kg^{-1}.

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $\lvert c_i \rvert$	Uncertainty contribution $u_i(y)$
E / V	0.464	2×10^{-5}	1	$2\text{x}10^{-5}$
T / K	298.15	8×10^{-3}	8.1×10^{-4}	6.7×10^{-6}
m_{HCl} / mol kg^{-1}	0.01	1×10^{-5}	5.14	5.1×10^{-5}
p_{H2} / kPa	101.000	0.003	1.3×10^{-7}	4.2×10^{-7}
Δ(Ag/AgCl) /V Bias potential	$3\cdot10^{-5}$	3.5×10^{-5}	1	3.5×10^{-5}
$g_\pm$	0.9042	9.3×10^{-4}	0.0568	5.2×10^{-6}

$u_c(E^0) = 6.5\times10^{-5}$ V

Note: The uncertainty of method used for the determination of hydrochloric acid concentration is critical. The uncertainty quoted here is for potentiometric silver chloride titration. The uncertainty for coulometry is about ten times lower.

Table A1b. Calculation of the standard uncertainty of the acidity function $\lg(a_H\gamma_{Cl})$ for m_{Cl} = 0.005 mol kg^{-1}

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $\lvert c_i \rvert$	Uncertainty contribution $u_i(y)$
E /V	0.770	2×10^{-5}	16.9	3.4×10^{-4}
E^0 /V	0.222	6.5×10^{-5}	16.9	1.1×10^{-3}
T /K	298.15	8×10^{-3}	0.031	2.5×10^{-4}
m_{Cl} / mol kg^{-1}	0.005	$2.2\times\cdot10^{-6}$	86.86	1.9×10^{-4}
p_{H2} /kPa	101.000	0.003	2.2×10^{-6}	7×10^{-6}
Δ(Ag/AgCl) /V	$3\cdot10^{-5}$	$3.5\text{x}10^{-5}$	16.9	5.9×10^{-4}

$u_c(\lg(a_H\gamma_{Cl})) = 0.0013$

Note: If, as is usual practice in some NMIs (42-44), acid and buffer cells are measured at the same time, then the pressure measuring instrument uncertainty quoted above (0.003 kPa) cancels but there remains the possibility of a much smaller bubbler depth variation between cells.

The standard uncertainty due to the extrapolation to zero added chloride concentration (§ 4.4) depends in detail on the number of data points available and the concentration range. Consequently, it is not discussed in detail here. This calculation may increase the expanded uncertainty (of the acidity function at zero concentration) to $U(k = 2) = 0.004$.

As discussed in § 5.2), the uncertainty due to the use of the Bates-Guggenheim convention includes two components:
(i) The uncertainty of the convention itself, and this is estimated to be approximately 0.01. This contribution to the uncertainty is required if the result is to be traceable to SI, but will not be included in the uncertainty of "conventional" pH values.
(ii) The contribution to the uncertainty from the value of the ionic strength should be calculated for each individual case.
The typical uncertainty for Cell I is between $U(k = 2) = 0.003$ and $U(k = 2) = 0.004$.

A 2 Uncertainty Budget for Secondary pH Buffer using Cell II

$^{-}\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{S_2} \;\vdots\; \mathrm{KCl}\ (\geq 3.5\mathrm{mol\ dm^{-3}}) \;\vdots\; \mathrm{S_1} \mid \mathrm{H_2} \mid \mathrm{Pt}$ Cell II

where S_1 and S_2 are different buffers.

A 2.1 Measurement Equations

1. Determination of $pH(S_2)$

$pH_{II}(S_2) - pH_{II}(S_1) = E_{II}/k - (E_{j2} - E_{j1})/k$ (A6) cf (9)

2. Theoretical Slope, $k = (RT/F)\ln 10$.

A2.3 Uncertainty Budget
Table A2
S1 = Primary buffer, pH(PS) = 4.005, u(pH) = 0.003; S2 = Secondary pH buffer, pH(SS) = 6.86
Free diffusion junctions with cylindrical symmetry formed in vertical tubes were used (25).

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $\lvert c_i \rvert$	Uncertainty contribution $u(y_i)$
pH (S_1)	4.005	0.003	1	0.003
E_{II} /V	0.2	1×10^{-5}	16.9	1.7×10^{-4}
$(E_{j2} - E_{j1})$ /V	3.5×10^{-4}	3.5×10^{-4}	16.9	6×10^{-3}
T / K	298.15	0.1	1.2×10^{-5}	1.2×10^{-6}

$u_c(pH(S_2)) = 0.007$

Note: The error in E_{II} is estimated as the scatter from 3 measurements. The RLJP contribution is estimated from Figure 2 as 0.006 in pH; it is the principal contribution to the uncertainty.

Therefore $U(k = 2)$, $pH(S_2) = 0.014$

A3 Uncertainty Budget for Secondary pH Buffer using Cell III

$$Pt|H_2|\text{Buffer } S_2 \,\vdots\, \text{Buffer } S_1|H_2|Pt \qquad \text{(III)}$$

A3.1 Measurement equations:

(1) $pH(S_2) - pH(S_1) = (E_{III} + E_j)/k$ (A7) cf. (11)

(2) $k = (RT/F)\ln 10$

For experimental details see (33), (38), (16)

Table A3

S_1 = Primary Standard (PS) and S_2 = Secondary Standard (SS) are of the same nominal composition. Example: 0.025 mol kg^{-1} disodium hydrogen phosphate + 0.025 mol kg^{-1} potassium dihydrogen phosphate, $PS_1 = 6.865$, $u(pH) = 0.002$.

pH (S_2) Determination

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $\lvert c_i \rvert$	Uncertainty contribution $u_i(y)$
pH (PS_1)	6.865	2×10^{-3}	1	2×10^{-3}
$(E(S_2)-E(S_1))$ /V	1×10^{-4}	1×10^{-6}	16.9	16.9×10^{-6}
$(E_{id}(S_2)-E_{id}(S_1))$ /V	1×10^{-6}	1×10^{-6}	16.9	1.7×10^{-5}
E_j /V	10^{-5}	1×10^{-5}	16.9	16.9×10^{-5}
T / K	298.15	2×10^{-3}	5×10^{-6}	1×10^{-8}

$u_c(pH\ (S_2)) = 0.002$

Therefore $U(k = 2)$, $pH(S_2) = 0.004$.
The uncertainty is no more than that of the primary standard PS_1.

Note: $(E_{id}(S_2)-E_{id}(S_1))$ is the difference in cell potential when both compartments are filled with solution made up from the same sample of buffer material. The estimate of E_j comes from the observations made of the result of perturbing the pH of samples by small additions of strong acid or alkali, and supported by Henderson equation considerations, that E_j contributes about 10% to the total cell potential (33).

A4 Uncertainty Budget for Secondary pH Buffer using Cell IV

$$Ag|AgCl\ |\ KCl\ (\geq 3.5 mol\ dm^{-3}) \,\vdots\, \text{Buffer } S_1 \text{ or } S_2|\ H_2\ |\ Pt \qquad \text{Cell IV}$$

A4.1 Measurement Equations

1. Determination of $pH(S_2)$

$pH_{IV}(S_2) - pH_{IV}(S_1) = -[E_{IV}(S_2) - E_{IV}(S_1)]/k - (E_{j2} - E_{j1})/k$ (A8) cf. (13)

2. Theoretical Slope, $k = (RT/F)\ln 10$

A4.2 Uncertainty Budget

Table A4
Example from work of Paabo and Bates (5) supplemented by private communication from Bates to Covington. S_1 = 0.05 equimolal phosphate; S_2 = 0.05 mol kg-1 potassium hydrogen phthalate. KCl = 3.5 mol dm^{-3}.

S_1 = Primary Buffer PS_1, pH = 6.86, u(pH) = 0.003, Secondary Buffer S_2 = 4.01.

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $\|c_i\|$	Uncertainty Contribution $u(y_i)$
pH(S_1)	6.86	0.003	1	0.003
ΔE_{IV}/V	0.2	2.5×10^{-4}	16.9	4×10^{-3}
$(E_{j2}-E_{j1})$ /V	3.5×10^{-4}	3.5×10^{-4}	16.9	6×10^{-3}
T / K	298.15	0.1	1.78×10^{-3}	1.78×10^{-4}

u_c(pH(S2) = 0.008

Note: The estimate of the error in ΔE_{IV} comes from an investigation of several 3.5 mol dm^{-3} KCl calomel electrodes in phosphate solutions. RLJP contribution for free diffusion junctions is estimated from Figure 2 as 0.006 in pH.

Therefore $U(k = 2)$, pH(S_2) = 0.016.

A5 Uncertainty budget for unknown pH(X) buffer determination using Cell V

Ag |AgCl | KCl (≥3.5mol dm^{-3}) ¦ Buffer pH(S) or pH(X) | glass electrode Cell V

A5.1 Measurement Equations: 2-point calibration (bracketing).

1. Determination of the practical slope (k')

$$k' = [(E_V(S2) - E_V(S1)]/[pH(S2) - pH(S1)] \quad \text{((A9) cf. (16)}$$

2. Measurement of unknown solution (X)

$$pH(X) = pH(S_1) - [E_V(X) - E_V(S_1)]/k' - (E_{j2} - E_{j1})/k' \quad \text{(A10) cp.(15)}$$

A5.2 Uncertainty Budget.
Example of two-point calibration (bracketing) with a pH combination electrode (47).

Table A5a
Primary Buffers PS_1 pH = 7.4, u(pH) = 0.003; PS_2 = 4.01, u(pH) = 0.003.

Practical Slope (k') Determination

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient $\|c_i\|$	Uncertainty contribution $u(y_i)$
ΔE / V	0.2	5×10^{-4}	2.95×10^{-1}	1.5×10^{-4}
T / K	298.15	0.1	1.98×10^{-4}	1.98×10^{-5}
$(E_{j2}-E_{j1})$ /V	6×10^{-4}	6×10^{-4}	2.95×10^{-1}	1.8×10^{-4}
ΔpH	3.39	4.24×10^{-3}	1.75×10^{-2}	7.40×10^{-5}

$u_c(k') = 2.3\times10^{-4}$

Table A5b pH(X) Determination

Quantity	Estimate x_i	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty contribution $u(y_i)$
pH (S_1)	7.4	0.003	1	0.003
ΔE /V	0.03	1.40×10^{-5}	16.95	2.37×10^{-4}
$(E_{j2}-E_{j1})$ /V	6.00×10^{-4}	6.00×10^{-4}	16.95	1.01×10^{-2}
k' /V	0.059	2.3×10^{-4}	9.01	2.1×10^{-3}

$u_c(\text{pH(X)} = 1.06\times10^{-2}$

Note: The estimated error in ΔE comes from replicates. The RLJP is estimated as 0.6 mV.

Therefore $U(k = 2)$, pH(X) = 0.021

A5.2 Measurement equations for multi-point calibration:

$$E_V(S) = E_V^o - k' \text{ pH(S)} \qquad \text{(A11) cf. (17)}$$

$$\text{pH(X)} = [E_V^o - E_V(X)]/k \qquad \text{(A12) cf. (18)}$$

Uncertainty budget:
Example: Standard buffers pH(S_1) = 3.557, pH(S_2) = 4.008, pH(S_3) = 6.865, pH(S_4) = 7.416, pH(S_5) = 9.182; pH(X) was a 'ready to use' buffer solution with a nominal pH of 7.
A combination electrode with capillary liquid junction was used. For experimental details see (41); and for details of the calculations see (45).

Table A5c

Quantity	Estimate x_i	Standard uncertainty u(x_i)	Sensitivity coefficient $\lvert c_i \rvert$	Uncertainty contribution $u_i(y)$
E^0 /V	-0.427	5×10^{-4}	16.96	0.0085
T/ K	298.15	0.058	1.98×10^{-4}	1.15×10^{-5}
E(X) /V	0.016	2×10^{-4}	16.9	0.0034
$k´$ /V	0.059	0.076×10^{-3}	67.6	0.0051

u_c(pH(X)) = 0.005

Note: There is no explicit RLJP error assessment as it is assessed statistically by regression analysis. The uncertainty is will be different arising from the RLJPs if an alternative selection of the 5 standard buffers were used. The uncertainty attained will be dependent on the design and quality of the commercial electrodes selected.

Therefore,$U(k = 2)$ pH(X) = 0.01

Table A6. Values of the relative permittivity of water (46) and the Debye-Hückel limiting law slope for activity coefficients as lg γ in eqn. (6). Values are for 100. 000 kPa but the difference from 101.325 kPa (1 atm.) is negligible.

Temp. ^oC	Relative Permittivity	A $mol^{-½}\,kg^{½}$
0	87.90	0.4904
5	85.90	0.4941
10	83.96	0.4978
15	82.06	0.5017
20	80.20	0.5058
25	78.38	0.5100
30	76.60	0.5145
35	74.86	0.5192
40	73.17	0.5241
45	71.50	0.5292
50	69.88	0.5345

14. Summary of Recommendations

- IUPAC recommended definitions, procedures and terminology are described relating to pH measurements in dilute aqueous solutions in the temperature range 0 -50 ^oC.

- The recent definition of *primary method of measurement* permits the definition of primary standards for pH, determined by a primary method (cell without transference, called the Harned cell) and of secondary standards for pH.

- pH is a conventional quantity and values are based on the Bates-Guggenheim convention. The assigned uncertainty of the Bates-Guggenheim convention is 0.01 in pH. By accepting this value, pH becomes traceable to the internationally accepted SI system of measurement.

- The required attributes (listed in § 6.1) for primary standard materials effectively limit the number of primary substances to 6, from which 7 primary standards are defined in the range pH 3 - 10 (at 25 ^{o}C). Values of pH(PS) from 0 –50 ^{o}C are given in Table 2.

- Methods that can be used to obtain the difference in pH between buffer solutions are discussed in §8. These methods include the use of cells with transference that are practically more convenient to use than the Harned cell, but have greater uncertainties associated with the results.

- Incorporation of the uncertainties for the primary method, and for all subsequent measurements, permits the uncertainties for all procedures to be linked to the primary standards by an unbroken chain of comparisons. Despite its conventional basis the definition of pH, the establishment pH standards and the procedures for pH determination are self consistent within the confidence limits determined by the uncertainty budgets.

- Comparison of values from the cell with liquid junction with the assigned pH (PS) values of the same primary buffers measured with Cell I makes the estimation of values of the residual liquid junction potentials (RLJP) possible (§7), and the consistency of the 7 primary standards can be estimated.

- The Annex (§13) to this document of recommendations includes typical uncertainty estimates for the 5 cells and measurements described, which are summarised in Table 4.

- The hierarchical approach to primary and secondary measurements facilitates the availability of recommended procedures for carrying out for laboratory calibrations with traceable buffers grouped to achieve specified target uncertainties of unknowns (§ 11). The three calibration procedures in common use, one-point, two-point (bracketing), and multi-point, are described in terms of target uncertainties.

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Table 1 Summary of Useful Properties of some **Primary** and Secondary Standard Buffer Substances and Solutions (5)

Substance	Molecular formula	Molality/ mol kg^{-1}	Molar mass/ g mol^{-1}	Density/ g dm^{-3}	Molarity at 20 °C/ mol dm^{-3}	Mass/g to make 1 dm^3	Dilution value $\Delta pH_{½}$	Buffer value (β) /mol OH^- dm^{-3}	pH Temperature coefficient /K^{-1}
potassium tetraoxalate	$KH_3C_4O_8.2H_2O$	0.1	254.191	1.0091	0.09875	25.101			
potassium tetraoxalate	$KH_3C_4O_8.2H_2O$	0.05	254.191	1.0032	0.04965	12.620	0.186	0.070	0.001
potassium hydrogen tartrate (sat at 25 °C)	$KHC_4H_4O_6$	0.0341	188.18	1.0036	0.034	6.4	0.049	0.027	- 0.0014
potassium dihydrogen citrate	$KH_2C_6H_5O_7$	0.05	230.22	1.0029	0.04958	11.41	0.024	0.034	- 0.022
Potassium hydrogen phthalate	$KHC_8H_4O_4$	0.05	204.44	1.0017	0.04958	10.12	0.052	0.016	0.00012
disodium hydrogen orthophosphate +	Na_2HPO_4	0.025	141.958	1.0038	0.02492	3.5379	0.080	0.029	- 0.0028
potassium dihydrogen orthophosphate	KH_2PO_4	0.025	136.085			3.3912			
disodium hydrogen orthophosphate +	Na_2HPO_4	0.03043	141.959	1.0020	0.08665	4.302	0.07	0.016	- 0.0028
potassium dihydrogen orthophosphate	KH_2PO_4	0.00869	136.085		0.03032	1.179			
disodium tetraborate	$Na_2B_4O_7.10H_2O$	0.05	381.367	1.0075	0.04985	19.012			
disodium tetraborate	$Na_2B_4O_7.10H_2O$	0.01	381.367	1.0001	0.00998	3.806	0.01	0.020	- 0.0082
sodium hydrogen carbonate +	$NaHCO_3$	0.025	84.01	1.0013	0.02492	2.092	0.079	0.029	-0.0096
sodium carbonate	Na_2CO_3	0.025	105.99			2.640			
calcium hydroxide (sat at 25 °C)	$Ca(OH)_2$	0.0203	74.09	0.9991	0.02025	1.5	-0.28	0.09	-0.033

Table 2 Typical Values of pH(PS) for Primary Standards at 0 - 50 ^{o}C (see § 6.2).

	Temp./ ^{o}C										
Primary Standards (PS)	0	5	10	15	20	25	30	35	37	40	50
Sat. potassium hydrogen tartrate (at 25 deg C)						3.557	3.552	3.549	3.548	3.547	3.549
0.05 mol kg^{-1} potassium dihydrogen citrate	3.863	3.840	3.820	3.802	3.788	3.776	3.766	3.759	3.756	3.754	3.749
0.05 mol kg^{-1} potassium hydrogen phthalate	4.000	3.998	3.997	3.998	4.000	4.005	4.011	4.018	4.022	4.027	4.050
0.025 mol kg^{-1} disodium hydrogen phosphate + 0.025 mol kg^{-1} potassium dihydrogen phosphate	6.984	6.951	6.923	6.900	6.881	6.865	6.853	6.844	6.841	6.838	6.833
0.03043 mol kg^{-1} disodium hydrogen phosphate + 0.008695 mol kg^{-1} potassium dihydrogen phosphate	7.534	7.500	7.472	7.448	7.429	7.413	7.400	7.389	7.386	7.380	7.367
0.01 mol kg^{-1} disodium tetraborate	9.464	9.395	9.332	9.276	9.225	9.180	9.139	9.102	9.088	9.068	9.011
0.025 mol kg^{-1} sodium hydrogen carbonate + 0.025 mol kg^{-1} sodium carbonate	10.317	10.245	10.179	10.118	10.062	10.012	9.966	9.926	9.910	9.889	9.828

Table 3 Values of pH(SS) of some Secondary Standards from Harned Cell I measurements

	Temp. / °C									
Secondary Standards	0	5	10	15	20	25	30	37	40	50
0.05 mol kg^{-1} potassium tetraoxalate[a] (5, 17)	1.67	1.67	1.67	1.67	1.68	1.68	1.68	1.69	1.69	1.71
0.05 mol kg^{-1} sodium hydrogen diglycolate[b] (31)		3.47	3.47	3.48	3.48	3.49	3.50	3.52	3.53	3.56
0.1 mol dm^{-3} ethanoic acid + 0.1 mol dm^{-3} sodium ethanoate (25)	4.68	4.67	4.67	4.66	4.66	4.65	4.65	4.66	4.66	4.68
0.01 mol dm^{-3} ethanoic acid + 0.1 mol dm^{-3} sodium ethanoate (25)	4.74	4.73	4.73	4.72	4.72	4.72	4.72	4.73	4.73	4.75
0.02 mol kg^{-1} piperazine phosphate[c] (32)	6.58	6.51	6.45	6.39	6.34	6.29	6.24	6.16	6.14	6.06
0.05 mol kg^{-1} tris hydrochloride + 0.01667 mol kg^{-1} tris[c] (5)	8.47	8.30	8.14	7.99	7.84	7.70	7.56	7.38	7.31	7.07
0.05 mol kg^{-1} disodium tetraborate	9.51	9.43	9.36	9.30	9.25	9.19	9.15	9.09	9.07	9.01
Saturated (at 25 °C) calcium hydroxide (5)	13.42	13.21	13.00	12.81	12.63	12.45	12.29	12.07	11.98	11.71

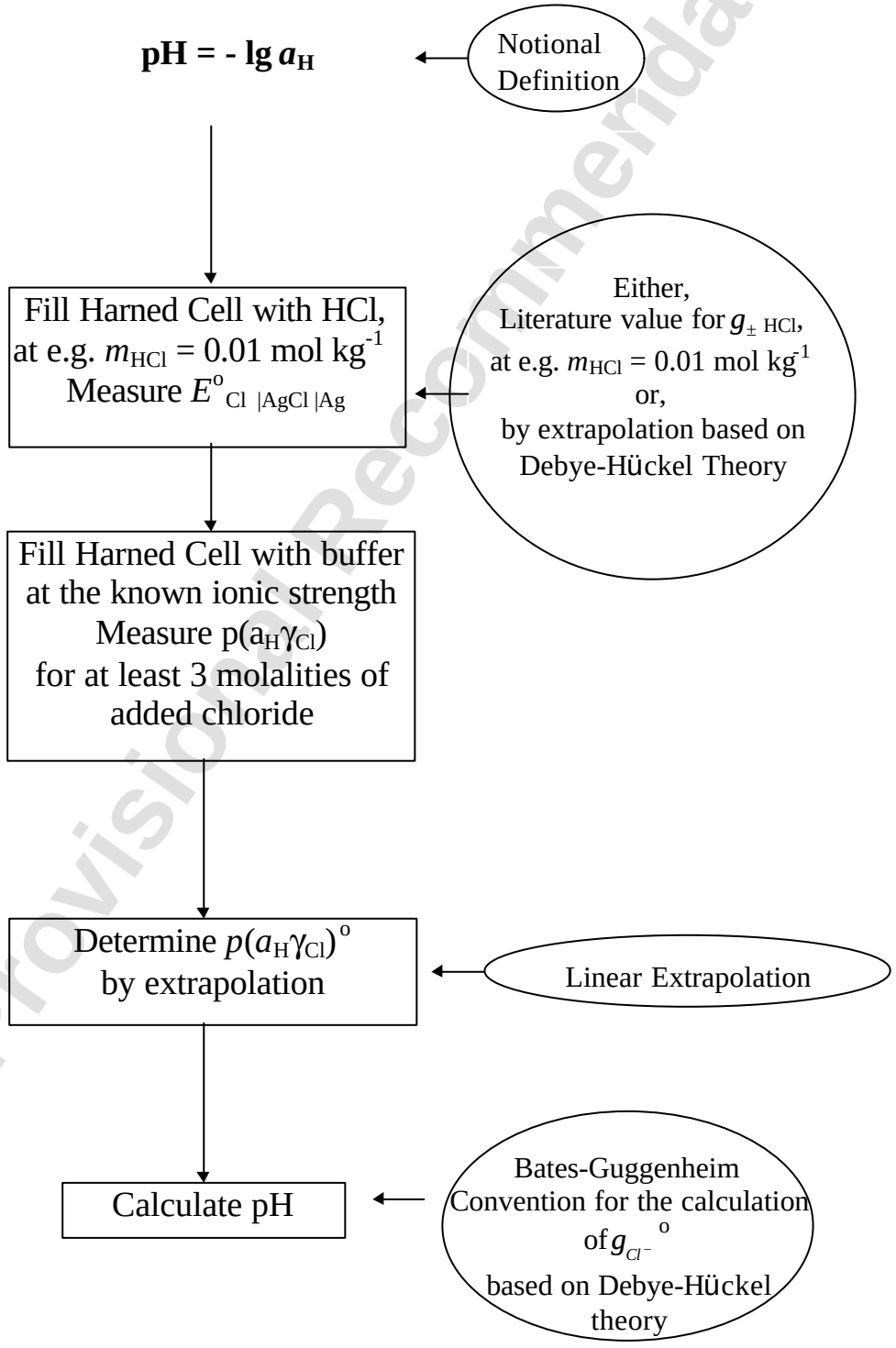
[a] potassium trihydrogen dioxalate ($KH_3C_4O_8$)
[b] sodium hydrogen 2,2' oxydiethanoate
[c] 2-amino-2-(hydroxymethyl)-1,3 propanediol or tris(hydroxymethyl)aminomethane

Table 4. Summary of Recommended Target Uncertainties

Primary Standards	U(pH) $k = 2$	Comments
Uncertainty of PS measured (by an NMI) with Harned Cell I	0.004	
Repeatability of PS measured (by an NMI) with Harned Cell I	0.0015	
Reproducibility of measurements in comparisons with Harned Cell I	0.003	EUROMET comparisons
Typical variations between batches of primary standard buffers	0.003	
Secondary Standards		
Value of SS compared with same PS material with Cell III	0.004	increase in uncertainty is negligible relative to PS used
Value of SS measured in Harned Cell I	0.01	e.g. biological buffers
Value of SS labelled against different PS with Cell II or IV	0.015	
Value of SS (not compatible with $Pt\|H_2$) measured with Cell V	0.02	example based on phthalate
Electrode Calibration		
Multi-point (5 point) calibration	0.01 - 0.03	
Calibration (2 point) by bracketing	0.02 - 0.03	
Calibration (1 point), ΔpH = 3 and assumed slope	0.3	

Note: None of the above include the uncertainty associated with the Bates-Guggenheim convention so the results cannot be considered to be traceable to SI (see § 5.2).

Fig. 1 **Operation of the Harned Cell as a Primary Method for the Measurement of Absolute pH**



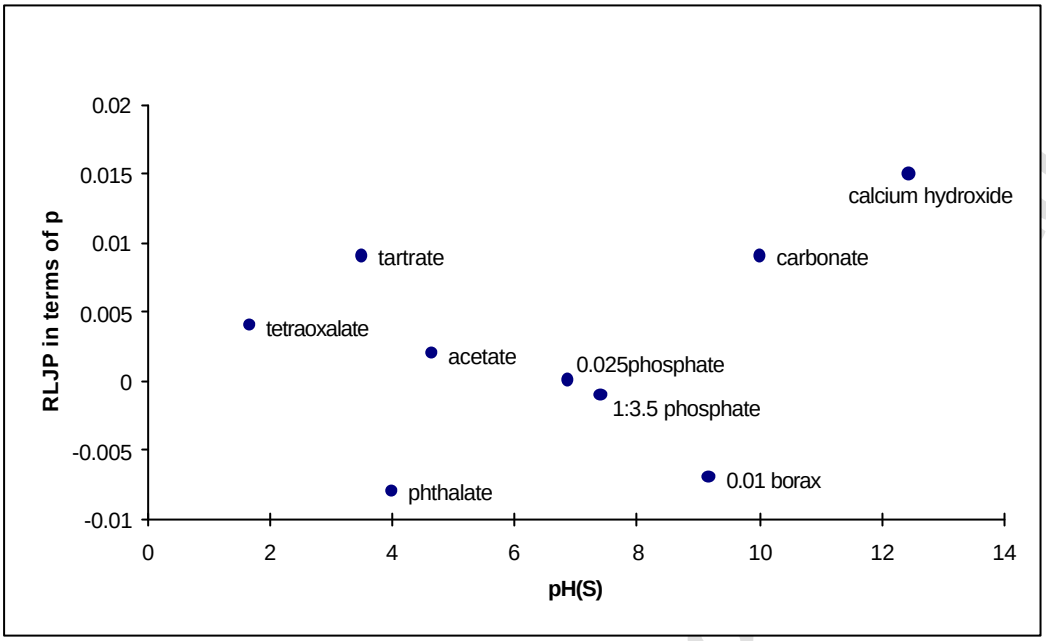


Figure 2. Some values of residual liquid junction potentials in terms of pH with reference to the value for 0.025 mol kg^{-1} Na_2HPO_4 + 0.025 mol kg^{-1} KH_2PO_4 (0.025 phosphate buffer) taken as zero (25).

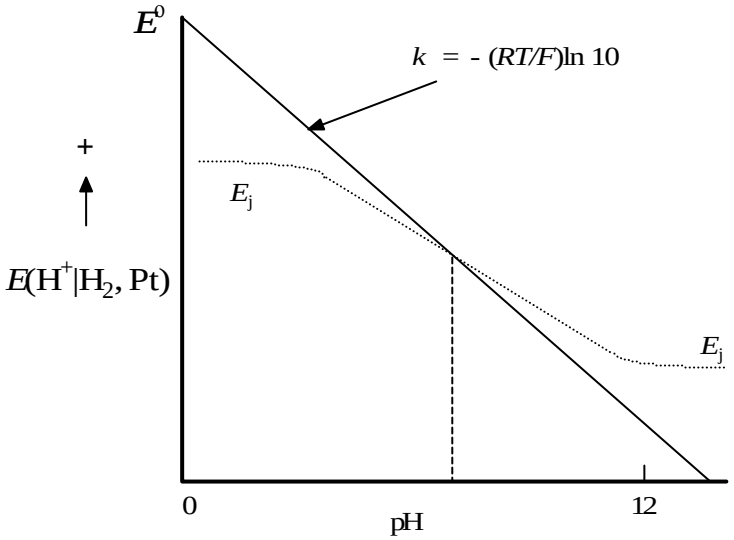


Figure 3. Schematic plot of the variation with pH of the potential difference (——) for the cell with liquid junction

$^{-}$ Ag | AgCl | KCl ¦ H^+(buffer S) |H_2 | Pt $^{+}$ Cell IV

illustrating the choice of sign convention.

The effect of liquid junction potential is indicated (–––) with its variation of pH as given by the Henderson equation (see e.g. ref. 5). The approximate linearityin the middle pH region should be noted. The line has been exaggerated in its deviation from the Nernst line since otherwise it would be indistinguishable from it.
For the calomel electrode Hg|Hg_2Cl_2|KCl or the thallium amalgam|thallium(I) chloride electrode Hg|Tl(Hg)|TlCl|KCl, or any other constant potential reference electrode, the diagram is the same.