Abstract  The IUPAC Recommendations on pH (1985) have serious metrological deficiencies (recommendation of two pH scales and of several pH definitions and procedures to measure pH). Background and essential features of new recommendations, which replace the 1985 document, are reported in this paper. The new document is strictly based on metrological principles. pH is defined (notionally) by the negative logarithm of the hydrogen ion activity according to Sørensen and Linderstrøm-Lang (1924), that is $\text{pH} = -\log_{10} a_H$. Because pH is a single ion quantity it is immeasurable and is therefore experimentally verified, with stated uncertainties, by pH(PS) values of primary standard buffer solutions. The assignment of pH(PS) is carried out in a Harned cell (without transference), which is defined as a primary method of measurement, and involves the Bates-Guggenheim convention. pH(PS) is thus a conventional quantity. Consideration of the uncertainty of the Bates-Guggenheim convention, however, permits its incorporation into the internationally accepted SI system of measurement. Comparison of the pH of secondary buffer solutions with pH(PS) values in recommended cells with transference yields secondary standards, whose pH(SS) can be traced back to pH(PS) and consequently to the definition of pH. The traceability chain is continued “downwards” by practical cells with transference containing glass electrodes for the measurement of pH(X) values of unknown solutions, for which three calibration procedures are recommended. The measurement of pH is thus represented by the traceability chain $\text{pH(X)} \rightarrow \text{pH(SS)} \rightarrow \text{pH(PS)} \rightarrow \text{pH}$ as defined, each step having stated uncertainties. This hierarchical system of measurement excludes any pH ‘scale’. Tabulated pH(PS) values are given as examples, and it is recommended that actual pH(PS) and pH(SS) be taken from certificates, which are to accompany each lot of certified reference material (CRM). Target uncertainties and examples of their calculation, a sign convention for pH cells and conventions for presenting cell schemes are given in the new document.

Keywords  IUPAC recommendations · pH definition · pH measurement · Traceability · Standard buffer solutions

Introduction

During the past four years, new recommendations on pH have been prepared by IUPAC. These are available on the Internet [1] and are scheduled to be published in print in the near future [2]. The new document will replace IUPAC Recommendations 1985 [3], which are highly unsatisfactory metrologically, since, inter alia, they recommend the use of two pH scales, the single standard and the multi-standard scale, and thus allow the measurement of two different pH values for each analysed solution. For this reason, they had been scheduled as an interim document from the beginning, which was to be replaced by amended recommendations when “a thermodynamically and metrologically sound pH scale can be recommended” [3]. Because such new insight, especially into the metrology of pH measurement, had been gained in 1997, an Inter-divisionary Working Party (WP) on pH was established [4], which consisted of members of IUPAC Commissions I.3 (Physical and Biophysical Chemistry Division), Commission Electrochemistry and V.5 (Analytical Chemistry Division, Commission Electroanalytical Chemistry) and experts from outside IUPAC. The WP thus consisted of extremely dedicated scientists (see authors of the new document [1]), and was charged with finally reaching a decision on the twenty-year-old controversy on pH measurement and to prepare new recommendations. The edi-
The new IUPAC recommendations are based on one definition of pH, the definition proposed by Sørensen and Lindberstrom-Lang in 1924 [7],

\[
\text{pH} = -\log a_H = -\log \left( \frac{m_H \gamma_H}{m^0} \right)
\]  

(1)

in which \( a \) is relative activity, \( m \) is molality, \( \gamma \) is activity coefficient and \( m^0 \) is standard molality (1 mol kg\(^{-1}\)). Assigned or measured practical pH values are linked to this definition by traceable procedures; traceability, according to internationally agreed upon standards (e.g. [8]) is the “property of a 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”. Traceability is thus the governing metrological principle of pH measurement, which, consequently, has eliminated any pH ‘scales’. Indeed, the term ‘scale’ is not mentioned in the new IUPAC recommendations.

Primary pH standards.

Absolute measurement of pH(PS)

According to international metrological principles, “a primary method of measurement has the highest metrological qualities, whose operation can completely be described and understood, for which a complete uncertainty statement can be written down in terms of SI units” [8]. In this sense, the term “absolute measurement” used in the section heading, which is also found in the new document, is to be understood to mean “without reference to other standards of the same quantity” and does not address the (notional) definition, as pH, as defined by Eq. (1), is measurable because it involves a single ion quantity, the hydrogen ion activity. The pH(PS) of primary standard solutions thus approaches the defined pH as closely as present electrolyte theory permits but is not necessarily identical to it.

The potentiometric cell that meets the metrological requirements of a primary method of measurement is the Harned cell [9],

\[
\text{Pt} \mid \text{H}_2 \mid \text{bufferS} \mid \text{Cl}^- \mid \text{AgCl} \mid \text{Ag}
\]

(1)

which has already extensively been applied for assigning primary standard pH values by Bates [10]. It qualifies because the potentials of both the PtH\(_2\) and the Ag|AgCl electrode obey the Nernst equation and correctly indicate the activities of hydrogen and chloride ions, respectively, and because the cell is without transference thus excluding liquid junction potentials. The buffer solution contains a small concentration of chloride, which is required for the functioning of the Ag|AgCl electrode. The effect of the chloride on the potential difference of cell I is eliminated by using at least three buffer solutions with varying chloride contents and by suitable extrapolation to zero added chloride concentration. The trace activity coefficient of chloride is then calculated by means of the extra-thermodynamic Bates-Guggenheim convention [11]. The resulting primary pH(PS) is a conventional quantity but can be incorporated into the internationally accepted SI system of measurement provided an uncertainty is assigned to the Bates-Guggenheim equation. The following paragraphs present the main equations of the assignment [1, 10] and show how pH can be introduced into the SI system according to the new document.

Application of the Nernst equation to the spontaneous cell reaction of cell I

\[
\frac{1}{2}\text{H}_2 + \text{AgCl} (s) \rightarrow \text{Ag} (s) + \text{H}^+ + \text{Cl}^-
\]

(2)

yields the potential difference

\[
E_I = E^0_{\text{Ag/AgCl}} - k \log \left( \frac{m_H \gamma_H}{m^0} \right) \left( \frac{m_{\text{Cl}} \gamma_{\text{Cl}}}{m^0} \right)
\]

(3)

(corrected to 101.325 kPa hydrogen partial pressure), where \( E^0_{\text{Ag/AgCl}} \) is the standard potential of the Ag|AgCl electrode (the standard potential of the PtH\(_2\) electrode is defined zero at all temperatures), and \( k = (RT/F) \ln 10 \), and rearrangement of Eq. (3) gives the so-called acidity function

\[
\text{p} (a_H \gamma_{\text{Cl}}) = -\log (a_H \gamma_{\text{Cl}}) = \frac{E_I - E^0_{\text{Ag/AgCl}}}{k} + \log \left( \frac{m_{\text{Cl}}}{m^0} \right)
\]

(4)

The standard potential of the Ag|AgCl electrode is obtained from the potential difference of the Harned cell when it is filled with 0.01 molal HCl and from published mean activity coefficients of this solution [12]. It is inserted into the acidity function, several values of which with different added chloride molality are then extrapolated to zero chloride molality by a linear extrapolation procedure,

\[
\lim_{m_{\text{Cl}} \to 0} \log (a_H \gamma_{\text{Cl}}) = \log (a_H \gamma_{\text{Cl}})^0 = \log a_H + \log \gamma_{\text{Cl}}^0
\]

(5)