

Measurement of pH: Definition, Standards, and Procedures. (IUPAC Recommendations 2002)

Pure and Applied Chemistry,
Vol. 74, No. 11, pp. 2169–2200 (2002)

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IUPAC Recommendations 2002 replace Recommendations 1985 (*Pure and Applied Chemistry* **57**[1985], 531–542), which are metrologically unsatisfactory and had been especially criticized for recommending two pH scales to measure two different pH values of any analyzed solution. This shortcoming had been realized by the experts, who, however, could not agree on one of the scales and recommended that the 1985 document be replaced by an amended document when “a thermodynamically and metrologically sound pH scale can be recommended.” An overview of this issue can be found in *Analytical and Bioanalytical Chemistry* **374**(2002), 772–777.

A new amended document, Recommendations 2002, strictly follows metrological principles. pH is defined (notionally) according to Sørensen and Linderstrøm-Lang (1924)

$$\text{pH} = -\lg a_{\text{H}} = -\lg (m_{\text{H}^+}/m^\circ)$$

(a = relative activity, m = molality, γ = molal activity coefficient, and m° = standard molality = 1 mol kg⁻¹), to which all assigned and measured pH values are traced back within stated uncertainties, thus securing an unbroken chain of comparison.

Because pH involves a single ion quantity, the hydrogen ion activity, it is immeasurable. It is therefore experimentally verified, with stated uncertainties, by primary standard pH(PS) values of primary standard buffer solutions (PS). The assignment is carried out in a cell without transference involving a Pt|H₂ electrode, the so-called Harned cell, which already has been extensively applied by Bates. It is defined a primary method of measurement and involves the Bates-Guggenheim convention. The new document states for the first time an estimated uncertainty of the Bates-Guggenheim convention, whose introduction into the conventional pH(PS) makes the incorporation of pH(PS) into the internationally accepted SI system of measurement possible. Seven buffer solutions qualifying as primary buffers are recommended. Their actual pH(PS) are to be certified by national metrological institutes (NMIs) and to be stated, together with their uncertainties, in certificates, which are to accompany the respective lots of the certified buffer materials. These pH(PS) values are to be used in prac-

tice, whereas pH(PS) values listed in a table of the document merely serve as examples. PS buffers are mainly applied by accredited laboratories for assigning secondary pH(SS) values to secondary standard buffers (SS).

For practical pH measurements, the application of SS buffers is more convenient. They do not meet the stringent requirements of PS or, if they do, are not assigned pH(PS) in a Harned cell for economic reasons. Since pH(SS) values are determined by comparison with pH(PS) values of primary buffers in cells with liquid junction (except for one case), their uncertainties are slightly larger, which is the reason for their status as secondary standards. Three cells are recommended for the assignment, and for each the typical uncertainty is given. The work is to be carried out by NMIs or accredited laboratories, which are to issue certificates containing the actual pH(SS) values. These certificates will then accompany the respective lots of the certified materials. The document presents several examples. SS buffers are applied whenever practical pH cells are calibrated.

Practical pH measurements are conducted in cells with liquid junction employing a glass electrode. They either contain the separate glass and reference electrodes or consist of their combination in so-called combination or single rod electrodes. Because of systematic and random effects of glass electrodes and liquid junction potentials, practical cells must be calibrated. The document recommends three—the one-point, two-point, and five- or multi-point calibration procedures—each of which has a characteristic uncertainty. Because the appropriate calibration procedure applied depends not only on the required target uncertainty of the measurement, it is not always possible to give a general rule for its choice.

The new recommendations are legally applicable because they yield one pH value, within stated uncertainties, for every analyzed dilute solution within the temperature range 0 to 50 °C. This is a most significant property and a true improvement over the 1985 document, which allowed the measurement of at least eight distinct, although not very different, pH values for each solution. Besides, pH is now part of the SI system of measurement, although this may be needed infrequently. The work of the Working Party on pH, which established the document through four years of dedicated work, was thus not only necessary, but also successful.



www.iupac.org/publications/pac/2002/7411/7411x2169.html