A Century of pH Measurements

Brewing and science, especially chemistry, have been intertwined throughout history. In fact, the pursuit of better beer and better methods for making it, have led to many scientific breakthroughs. One of the most important of these from a chemistry perspective was Søren Peder Lauritz Sørensen's introduction of the concept of pH, a quantity that is a measure of acidity and basicity. In 1909, Sørensen (1868–1939), a Danish biochemist and director of the research laboratories (Holter 1976) of Carlsberg Breweries in Copenhagen, developed a pH numerical scale as a simple way of expressing hydrogen ion concentrations, which he had realized played a key role in enzymatic reactions.*

Nowadays, most of the things we use on a daily basis, like tap water, food and beverages, cosmetics, and medicines, are tested for pH. And, of course, many chemical and biochemical processes are pH dependent. With the 100th anniversary of the introduction of the concept of pH, it is interesting to look back at the development of this important concept.

Pedr Sørensen titrating using an original set of buffer solutions and indicators.

by Maria Filomena Camões

In 1884, Svante Arrhenius (1859–1927) affirmed his Theory of Electrolytic Dissociation and produced the first definition of an acid based on its chemical composition and on its ability to dissociate in aqueous solution with the production of hydrogen ions, H^+ (Arrhenius, 1912). For the first time, a base was considered to be a substance that dissociated in water into hydroxyl ions, OH^-, and not simply to be a substance that opposed the effects of an acid. Concentration of hydrogen ions (c_H) may span over several orders of magnitude, from relatively high values, (e.g., above 1 mol dm^{-3} [= 10^0 mol dm^{-3}]), as is the case with concentrated solutions of strong mineral acids, to low values expressed in terms of powers of 10 with a negative exponent (e.g., 10^{-12} mol dm^{-3} for concentrated solutions of strong bases).

Even before defining pH, Sørensen had conducted pioneering research on the synthesis of aminoacids, on the preparation of reference buffer solutions, and on the colorimetric assessment of acidity (Sørensen 1907). For practical reasons, Sørensen defined pcH as the negative logarithm of hydrogen ion concentrations. This negative exponent, $c_H = 10^{-pcH}$, is numerically the same as the decadic logarithm of hydrogen ion concentration, $pcH = -\lg c_H = -\lg 10^{-pcH}$. The choice of "pH" was simply because it stood for ***p**ondus Hydrogenii*, although in other languages it could stand for **p**ower, **p**otenz, **p**otence, etc.

Most often, concentration values lie between 1 mol dm^{-3} and 10^{-14} mol dm^{-3}, with defined pH values of 0 and 14, respectively. Nevertheless, and despite the relatively common misconception that there are only values of pH above 0, negative pH values can be found in nature (e.g., in extremely acidic mine waters).

While conducting research on the effect of ion concentrations in the analysis of proteins, Sørensen noticed a color change of some acid-base indicators, produced in the presence of proteins, suggesting a pH shift, usually toward more alkaline values. (Rosenfeld 1999). This "protein error" allows protein detection by means of paper strips impregnated with buffered indicator: with constant pH, the indicator presents one color in the absence of proteins and a different one in their presence. For this reason and because many physiological processes depend upon pH, it is not sur-

* Complete references for this article can be found at <www.iupac.org/publications/ci/2010/3202/1_mfcamoes.html>.

prising that the first survey article on pH, published by L. Michaelis, mentioned the importance of hydrogen ion concentration and its measurement for biology (Michaelis 1914).

Having a conceptual definition of pH is one thing, but having an experimental realization of the defined quantity and the assignment of a pH value to a certain solution is another matter. As Sørensen and others found, colorimetric detection with color indicators does not allow sensitivity to pH changes better than 0.5, making the method unsuitable for demanding chemical objectives.

Together with his definition, Sørensen proposed an electrometric procedure for the evaluation of this quantity based on the measurement of the potential, $E_{H+/H2}$, of the platinum-based, Pt,H_2, (or palladium-based, Pd,H_2) hydrogen gas electrode, sensitive to hydrogen ions (H^+) that had been developed by LeBlanc (LeBlanc 1893). A thin foil of platinum electrolytically coated with a finely divided deposit of platinum or palladium metal, in solutions saturated with hydrogen gas, catalyzes the electrode reaction:

$$H^+ + e^- \rightarrow \tfrac{1}{2}\, H_2$$

This Pt-based (or Pd-based) hydrogen gas electrode is universally accepted as the primary standard, SHE, with which all other electrodes are compared. This is because it meets the requirements of reversibility and reproducibility (Hills 1961) for an arbitrary reference point of a numerical scale of potentials in aqueous media ($E_{H+/H2}{}^{o} = 0$ V, at all temperatures and for standard conditions of hydrogen gas pressure and hydrogen ion composition).

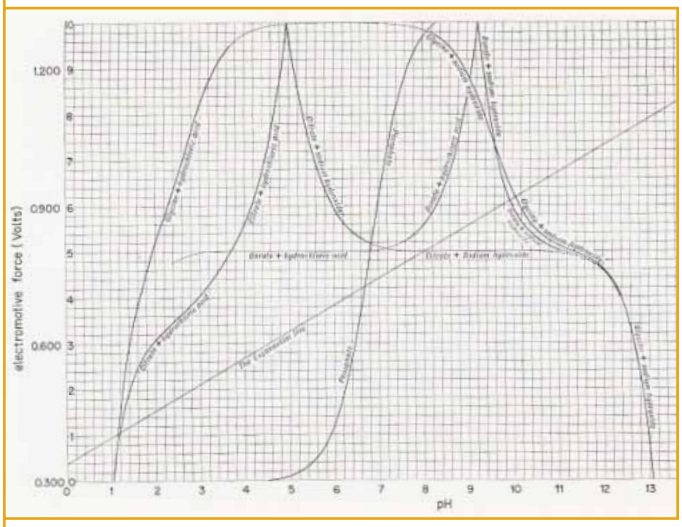

Chart of Sorensen buffer systems, which for many years acted as the standard for the definition of pH. The system consists of a succession of paired solutions, mixed in the quantities indicated by the ordinates to the right and left. The pH values of the resulting mixtures are given on the abscissa.

In practice, no single electrode potential can be independently assessed and only differences of potential between two electrodes can be calculated. Sørensen proposed that the pH of an unknown solution (X) is obtained from the potential, E (measured in potentiometric conditions; i.e., null current) of a cell previously developed by Bjerrum (Bjerrum 1906), represented below in terms of conventional notation:

$$Pt,H_2 \,|\, \text{Sol. } (c_H)_x \,||\, \underset{\text{Bridge}}{\text{Salt}} \,||\, 0.1 \text{ mol dm}^{-3} \text{ KCl} \,|\, Hg_2Cl_2, Hg$$

formed by combining two half-cells, one containing the platinum-based hydrogen-gas electrode (Pt,H_2), interfacing with a solution containing hydrogen ions, and the other one based on a calomel electrode (Hg,Hg_2Cl_2) sensitive to chloride ions (Cl^-) present in the solution it interfaces with, introduced by Ostwald (Ostwald 1894). A salt bridge establishes electrolytic contact between the solutions of the two half cells.

The empirical Nernst equation was used as the analytical law:

$$E_1 - E_2 = \frac{RT}{F} \ln \frac{(c_H)_2}{(c_H)_1} = \frac{RT \ln 10}{F} \lg \frac{(c_H)_2}{(c_H)_1}$$

E_1 and E_2 are the cell potentials at concentrations $(c_H)_1$ and $(c_H)_2$ respectively. R is the gas constant, F is the Faraday constant, and T is the absolute temperature. There is a linear relation between potential, E, and pH; the slope of the straight line, RT ln 10/F (change of potential when the concentration changes by tenfold) is known as the Nernst slope, equal to 59.16 mV at 25 °C (Szabadváry 1993).

Analytical laws, that relate the measured signal with the concentration of the envisaged analyte, namely the theoretical Nernst equation for the hydrogen ion, are strictly observed for ideal systems. Hence, in practical terms, deviations are likely to occur due to interactions between the species present in the systems. With the development of Gibbs Thermodynamics and Lewis's concept of activity of a chemical species, a_i, it became apparent that analytical laws, which relate a measured signal with the concentration of the envisaged analyte, are strictly observed in ideal systems (Lewis 1908). Both quantities, activity and concentration, are related through a conversion factor, the activity coefficient, γ_i,

concentration and matrix dependent. Potentiometric measurements are capable of supplying activity coefficients from certain well-defined experiments; in cases where concentration is known, comparisons between calculated and measured Nernst potential have been used to assess activity coefficients. Sørensen redefined pH= - lg a_H.

The new formulation of the Nernst equation and the awareness of the contribution of unknown liquid-liquid junction potentials made Sørensen and K. Linderstrøm-Lang recognise that the proposed experimental procedure did not lead to pH= -lg c_H, nor to pH= - lg a_H, but to some other quantity—psH—that, although merely convenient, was widely accepted by the scientific community.

With the hydrogen electrode immersed in 1 mol dm^{-3} HCl, with H_2 bubbling at 1 atm and 18°C, Sørensen reported a cell potential of 0.338 V against which an extensive number of buffer solutions had their psH values assigned from the measured corresponding potential, E

$$\text{p}s\text{H} = \frac{E\text{-}0{,}338}{0.05916} \quad (\text{at } 25^{\circ}\text{C})$$

The concept of pH corresponds only to a notional definition and is unique in the sense that it involves a single ion quantity, the activity of the hydrogen ion (Sørensen 1924), which does not exist on its own and is therefore immeasurable by any thermodynamically valid method. Its evaluation requires extra-thermodynamic conventions.

The procedure conventionally adopted to assign primary standard pH values (pH[PS]) to primary standard pH buffer solutions (PS) is based on the cell without transference, which is known as the Harned [Harned, 1958] cell:

$$\text{Pt} \mid \text{H}_2\,(1\text{ atm}) \mid \overset{\text{reference}}{\text{buffer solution}};\ \text{KCl}\,(m) \mid \text{AgCl} \mid \text{Ag}$$

It is composed of the Pt-based (or Pd-based) hydrogen gas electrode and the silver-silver chloride electrode, immersed in the reference buffer solution under study, with added potassium chloride (m_{KCl}= 0.005; 0.01; 0.015 mol kg^{-1}) in order to ensure proper working conditions of the silver-silver chloride electrode (figure 1). It was developed by R.G. Bates and collaborators (Bates 1973) at the U.S. National Bureau of Standards (later changed to the National Institute of Standards and Technology). It has been slightly modified by national metrological institutes around the world to comply with the requirements of a primary method.

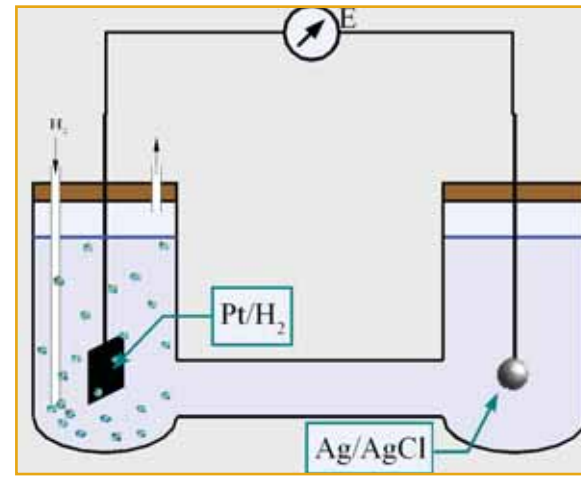

Figure 1. Schematic representation of the Harned Cell (Adapted from Petra Spitzer/PTB, Germany).

The application of the Nernst equation to the spontaneous cell reaction

$$\tfrac{1}{2}\,\text{H}_2 + \text{AgCl} \rightarrow \text{Ag(s)} + \text{H}^+ + \text{Cl}^-$$

and to the cell potential, E, is the starting point of a conventional procedure which, in an intermediate step, defines an acidity function, p(aH γCl), in terms of experimentally accessible quantities that are still free from assumptions. This is the reason why it is often reported and used in comparative studies. The adoption of the Debye-Hückel model of ionic interaction in electrolytic solutions (Debye 1923) led to the final assignment of the conventional pH value. This was made possible by the introduction of the Bates-Guggenheim convention for the activity coefficient of the chloride ion (Bates 1960), with an assigned uncertainty of 0.01 in pH. Determination of activity coefficients, γ_i, may also be calculated by means of the Pitzer theory (Pitzer 1991) in which specific ion interactions are taken into account enabling the calculation of pH values, and related quantities, for more complex media.

Quantitative interpretation of measured pH values is limited to dilute aqueous solutions of simple solutes. This requirement presents limitations to the nonaqueous media, suspensions, colloids, and aqueous solutions of ionic strength greater than 0.1 mol kg^{-1}, for which further considerations are necessary.

The definition of this procedure as the primary method of measurement has permitted the designation of a set of seven primary standard solutions for pH, pH(PS), (Bates 1973) from among those with the "highest metrological" quality (VIM 3, 2008).

The Potentiometric Method using the Pt– (or Pd–) based hydrogen gas electrode is the method for the assignment of pH values accepted by research and laboratory work necessitating accurate and precise pH measurements (except in those cases where the presence of certain classes of substances in the solution interfere with the measurement of the potential of the half-cell containing the hydrogen gas electrode). Despite the merits of the hydrogen gas electrode, it is certainly not practical for routine measurements. The discovery by Cremer, in 1906, of the selectivity of the reliable and accessible glass electrode toward H^+ (Cremer 1906) was a significant milestone for the practical measurement of pH.

A glass electrode is usually made by sealing a bulb about 0.2 mm thick of a silica glass containing metal oxides that break the structure of the glass at some points, and then fusing it onto a stem of electrically insulating glass. For many years, the best H^+ responsive glass available was composed of Na_2O (21.4 mol%), CaO (6.4%), and SiO_2 (72.2%), known as Corning 015 glass, whose potential followed the Nernst equation between pH 1 and 9. Several changes have been introduced in glass compositions in order to enhance desirable properties of the glass electrode, but no glass electrode yet constructed has the theoretical response in all types of solutions and over the entire practical pH range. On soaking the glass bulb in water, further breaking of the structure occurs and the open spaces are filled with water molecules from the solution, producing observable swelling. A gel-layer with hydrogen ions is created, which sets up a difference in potential across the glass-solution boundary, thereby developing a hydrogen function of the glass.

Other hydrogen ion sensors have been developed, but none surpass the glass electrode as demonstrated by Hughes' comparative studies between glass and hydrogen gas electrodes (Hughes 1922). Deviations occur for both the acidic region and for the alkaline region, which is the consequence of selectivity to alkaline and alkaline–earth cations (Eisenman 1967; Camões 1974).

The glass bulb has two surfaces. The outer surface is in contact with the solution whose pH is to be measured. The inner surface is kept in contact with a solution of constant pH, 0.1 mol dm^{-3} HCl, in which an internal silver-silver chloride electrode is immersed, providing electrical connection and a stable potential during measurements. Measurements of cell potentials also require an external reference electrode, usually silver-silver-chloride, Ag,AgCl. Combination electrodes (figure 2) in which the glass electrode and the external reference electrode are assembled together are commercially available and extensively used. Owing to the high electric resistance of glass, on the order of MΩ, measurements of potentials required a detecting element operating on a very small current that depended on the development of current amplifiers. The first commercially successful electronic pH meter was invented by Beckman (Beckman 1950). This set the foundation for the potentiometric determination of pH by combination glass electrodes and microprocessor pH meters currently in use (Covington 1985).

$$\text{Glass electrode} \,|\, \text{buffer solution} \,||\, \text{KCl} \geq 3.5 \text{ mol dm}^{-3} \,|\, \text{Ag,AgCl}$$

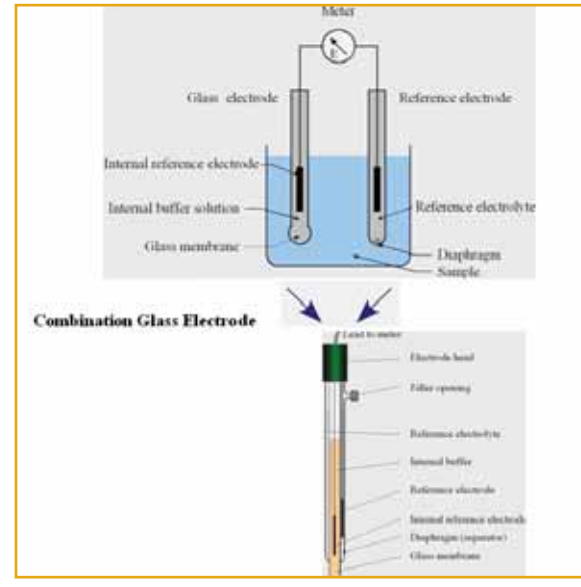

Figure 2. Glass electrode assembly (Adapted from Petra Spitzer/PTB, Germany).

Practical pH measurements generally use these working cells with liquid junctions that are practical, but have greater uncertainties associated with the results.

To use a glass electrode to measure pH of unknown solutions requires calibration. This is done by prior measurement of the working cell potential in pH standard buffer solutions of known pH, such as the typical NBS/NIST, or others specifically recommended for the particular characteristics of the sample (e.g., physiological fluids and seawater).

The hierarchical approach to measurements facilitates (Buck 2002) laboratory calibrations to achieve specified target uncertainties that are self consistent within the uncertainty budgets (De Bièvre 2009). This way, and despite the conventional definition of pH, values will become traceable to the internationally accepted SI system. This is a vexing problem that the scientific community has had difficulty solving.

Everyday chemical and biochemical processes are controlled via pH measurements. It is most likely the most measured chemical parameter and the one most people hear or talk about. The fact that pH meters are widely available at relatively low cost and that measurements are quite straightforward, even for those with no professional training, has resulted in the misconception that all is known and clear about pH. In fact, beyond the simple process of measuring pH, there is poor understanding of the concept, the basis for its derivation, and limitations of its applicability. Despite the various fundamental drawbacks, potentiometric pH measurements are popular, easy, sensititive, reliable, important, and useful, and will continue to be performed. Educational approaches regarding this topic should be improved, particularly at the introductory school level.

As we celebrate the centenary of Sørensen's first definition of pH, the following quote is worth considering:

"pH measurement is often deceptively easy . . . pH measurement can also be exasperatingly difficult."
—G. Mattock, 1963

Maria Filomena Camões <mfcamoes@fc.ul.pt> is a professor at Universidade de Lisboa and a member of the IUPAC Analytical Chemistry Division. She is task group chair of the project Comparable pH Measurements by Metrological Traceability.

www.iupac.org/web/ins/2004-005-2-500

Stamps International

See also www.iupac.org/publications/ci/indexes/stamps.html

Giant Sulfur Bacteria

A remarkable discovery, an unknown bacterium about 100 times larger than most common bacteria and big enough to be seen with the naked eye, was made in oxygen-depleted marine sediments off the coast of Namibia in Southeastern Africa in April 1997. A true giant among unicellular microorganisms, *Thiomargarita namibiensis* was found forming delicate strings of pearly spheres, some growing up to three-quarters of a millimeter in diameter. In addition to its abnormal size, this fascinating microbe is unusual in several other ways, including its ability to accumulate large quantities of nitrate ions within the cell, sometimes in concentrations 10 000 times higher than in the surrounding seawater. Significantly, nitrate is used to oxidize sulfide ions derived from the degradation of organic matter by sulfate-reducing bacteria, a process that constitutes the key source of energy for the cells and nicely links the natural cycles of nitrogen and sulfur.

The stamp illustrated in this note is part of a set issued by Namibia in 2003 to celebrate recent biological discoveries in the country, including a new species of catfish and an insect long thought to be extinct. The stamp features a photomicrograph of three cells of *Thiomargarita*, each about 0.2 mm in diameter, and is similar to the one depicted on the cover of the 16 April 1999 issue of *Science*, where the finding was initially disclosed. The small yellow dots are globules of elemental sulfur formed by the oxidation of sulfides and are deposited only in the thin outer layer of the cell—comprising only 2 percent of the cell's volume—that surrounds the large central reservoir of nitrate ions. Although a proposal to use *Thiomargarita* in the future to clean up pollution caused by agricultural nitrate-rich effluents may be far fetched, it is clear that the role that such sulfur bacteria play in the ecology of coastal waters should not be underestimated.

Written by Daniel Rabinovich <drabinov@uncc.edu>.