

Notes from the Oesper Collections

The Youden pH Meter

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In 1909 the Danish biochemist, Søren Peter Lauritz Sørensen (figure 1), introduced the concept of *pH* in the course of his electrometric study of the role of the aqueous hydrogen ion in the behavior of enzymes (1, 2). Sørensen used a “hydrogen” or $H^+/Pt/H_2$ anode, combined with a constant potential calomel cathode, in his study. The chemistry of the hydrogen electrode is described by the half-cell reaction (3):



and its potential, in keeping with the Nernst equation, by the expression:

$$E = -2.3(RT/F)\log[H^+] \quad [2]$$

when the pressure of the H_2 gas is fixed at 1 atmosphere (4). As may be seen, under these conditions the electrode potential is directly proportional to $-\log[H^+]$ and it is this quantity that became known as the *pH* of the solution:

$$pH = -\log[H^+] \quad [3]$$

Sørensen used a slide-wire potentiometer to make his *pH* measurements. Here a known potential is applied to counterbalance the potential of the hydrogen cell (i.e. the hydrogen electrode plus the calomel counter electrode) and to reduce its current output to zero, at which point the value of the applied counter-potential is equal to that of the cell potential. Since the point of balance is indicated by a galvanometer reading of zero, this technique became known as the “null-point method” and would form the basis of most commercial *pH* meter design for almost 40 years.

By 1920 *pH* was becoming sufficiently important to biochemists that various laboratory supply houses began offering to sell, as a single package, all of the electrical and electrode components required to make the necessary electrometric measurements (figure 2). Not unexpectedly, it was not long before it was realized that all of these electrical components could be housed in a single convenient box, thus giving rise to what most chemists now think of as the modern *pH* meter (5-8).



Figure 1 Søren Peter Lauritz Sørensen (1868-1939). An autographed portrait from our print and photo collections.

From this point on, the evolution of the meter itself was largely an issue of improved electronics rather than chemistry, though the latter would continue to play an important role in the choice of the electrodes used. As it turned out, the hydrogen electrode is not very convenient to work with. It requires a tank of ultra pure hydrogen gas and the necessary equipment to regulate both the pressure and flow rate. Equilibration times are slow and the Pt, which not only conducts the current but is also an essential catalyst for the electrode reaction itself, is susceptible to catalytic poisoning by various solutes and can also act as a surface for the competing electrochemical reduction of others.

These problems led to a search for alternative

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4882. H-ion Outfit, with diagrammatic illustration of connections.

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The outfit is as follows, the component parts of which are sold separately under their respective catalogue numbers. The prices indicated are those in effect October 10th, 1922, and are subject to change without notice:—

| | | | |
|---|--------|--|-------|
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| 4796. Lamp and Scale Galvanometer, L. & N. | 50.00 | 4992. Storage Battery | 6.00 |
| 4797. Lamp Resistance for 4796, for 110 volts | 5.00 | 4954. Clark Hydrogen Electrode Vessels (2) | 51.00 |
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| | | 4934. Calomel Electrode Vessel | 40.00 |
| | | 4565. Clark Connecting Vessel | 6.50 |
| | | 9374. Switch, single pole double throw | .25 |

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Figure 2. A circa 1922 ad for the various components required for the electrometric determination of pH using a hydrogen electrode as offered by the Arthur H. Thomas Co. of Philadelphia.

electrode systems among which was the so-called quinhydrone electrode, first proposed by the Danish chemist, Einar Biilmann, in 1921 (9, 10). As shown in figure 3, quinhydrone is actually a 1:1 charge-transfer complex of hydroquinone [C₆H₄(OH)₂] and benzoquinone [C₆H₄O₂] and dissociates into an equimolar mixture of these two components upon dissolution in water. Its use in a pH-sensitive electrode is based on the

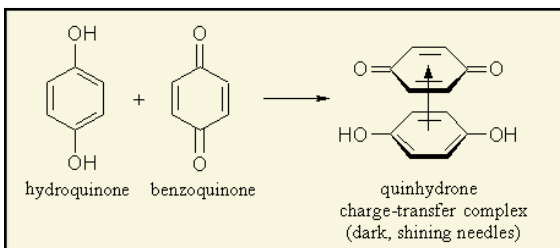
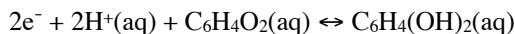


Figure 3. The structure of quinhydrone.

half reaction:



in which two C atoms are formally reduced from C(II) to C(I).

A typical cell arrangement proposed by Moir in 1931 is shown in figure 4 (11). This consists of three test tubes. Tube B in the center contains a saturated KCl solution and functions as a reservoir for the two KCl-agar salt bridges that connect the terminal tubes. Tube A on the right is the reference electrode and contains quinhydrone buffered with potassium hydrogen phthalate to maintain a constant H⁺(aq) concentration. Tube C on the left is the working electrode and contains quinhydrone dissolved in the solution to be tested. Here the H⁺(aq) concentration is determined by the nature of the test solution and so the net cell potential is in effect determined by the difference in the H⁺(aq) concentrations for the unknown versus the standard. Like the hydrogen cell, the quinhydrone cell also has some drawbacks. It is effective only for pH values less than 8, is susceptible to attack by strong oxidizing and reducing agents, and does not respond well to the presence of proteins.

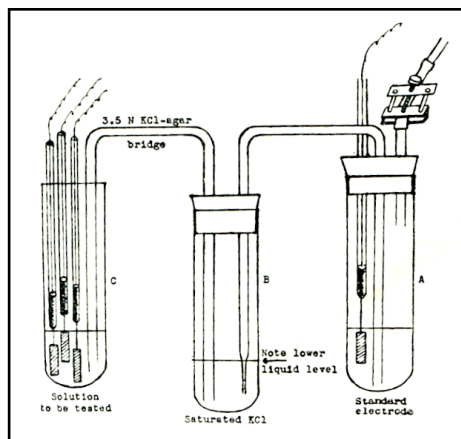


Figure 4. Arrangement of the quinhydrone electrode proposed by Moir in 1931 and used with the Youden pH meter.

A third electrode, known as the glass electrode, was first studied in detail by Haber and Klemensiewicz in 1909 (12, 13). It consists of a Ag/AgCl electrode immersed in a chloride solution that is surrounded by a thin glass membrane. It works on ion exchange between the H⁺(aq) ions in the surrounding solution and various metal ions in the glass. Because the internal components are protected by the glass membrane it is much less susceptible than either the hydrogen or quinhydrone electrodes to chemical interference from

THE YOUDEN pH METER



Figure 5. The Youden pH meter as advertised in the 1949 catalog for the W. H. Welch Scientific Co. of Chicago.

other species in the solution being tested. However, unlike these alternative electrodes, the glass electrode has a very high internal resistance and so produces a very weak cell current. Before it can be effectively used with a null-point instrument, its current must be amplified. This was initially done, starting in the late 1920s, using a De Forest triode vacuum tube and later more sophisticated amplification systems. Eventually it was possible to make the current output from the amplification strong enough, and sufficiently linear with respect to the cell potential on the grid, that it could be taken as a direct measure of the *pH*, thus giving rise to the so-called continuous or “direct-reading” commercial *pH* meter that became dominant starting in the 1950s.

The Oesper Collections own roughly fifteen *pH* meters spanning the period 1937-1975, about half of which are null-point instruments and half direct-reading instruments. They include examples manufactured by such companies as Beckman, Colman, Radiometer, Photovolt and Corning. All of them are designed for use with a glass electrode. However, thanks to the generosity of Dr. Richard A. Paselk of Humboldt State University, we have recently acquired a circa 1945 Youden null-point *pH* meter with a quinhydrone electrode system (figures 5 and 6). This is included in a black Bakelite case about a third the size of the meters made during this same period by Beckman and Colman and uses an electrode arrangement similar to that pro-



Figure 6. Our recently acquired Youden null-point pH meter. The Moir electrode system, minus one of the salt bridges, is to the left and a circa 1940 bottle of quinhydrone is displayed between it and the meter.

posed by Moir. This size reduction is due to the fact that the quinhydrone electrode does not require electronic amplification and the fact that, unlike the corresponding Beckman and Colman null-point instruments, the standard cell used to generate the counter-potential is connected externally via the binding posts on the extreme right rather than being inclosed within the case itself.

References and Notes

1. W. B. Jensen, "The Symbol for pH," *J. Chem. Educ.*, **2004**, *81*, 21.
2. S. Sørensen, "Enzymstudien II: Über die Messung und die Bedeutung der Wasserstoffionkonzentration bei enzymatischen Prozessen," *Biochem. Zeit.*, **1909**, *21*, 131-200.
3. In Sørensen's day half-cell reactions were written as oxidations rather than as reductions.
4. Recall that for the hydrogen electrode $E^\circ = 0$ by definition and $z = 1$.
5. J. J. Bohning, "pH Meter" in R. Bud, D. J. Warner, Eds., *Instruments of Science: An Historical Encyclopedia*, Garland: New York, NY, 1998, pp. 454-456.
6. B. Jaseskis, C. E. Moore, A. von Smolinski, "Development of the pH Meter," in J. T. Stock, M. V. Orna, Eds., *Electrochemistry, Past and Present*, American Chemical Society: Washington DC, 1989, pp. 254-271.
7. C. E. Moore, B. Jaseskis, "The pH Meter: A Product of Technological Crossovers," *Bull. Hist. Chem.*, **1998**, *21*, 32-36.
8. W. G. Hines, R. de Levie, "The Early Development of Electronic pH Meters," *J. Chem. Educ.*, **2010**, *87*, 1143-1153.
9. E. Biilmann, "Sur l'hydrogenation des quinhydrone," *Ann. chim.*, **1921**, *15*(series 9), 109-157.
10. J. T. Stock, "Einar Biilmann (1873-1946): pH Determination Made Easy," *J. Chem. Educ.*, **1989**, *66*, 910-912.
11. G. M. Moir, "The Use of the Quinhydrone Electrode," *Analyst*, **1931**, *56*, 445-448.
12. F. Haber, Z. Klemensiewicz, "Über elektrische Phasengrenzkräfte," *Z. physik. Chem.*, **1909**, *67*, 385-431.
13. C. E. Moore, B. Jaseskis, A. von Smolinski, "Development of the Glass Electrode," in J. T. Stock, M. V. Orna, Eds., *Electrochemistry, Past and Present*, American Chemical Society: Washington DC, 1989, pp. 272-285.