

## THE pH METER, A PRODUCT OF TECHNOLOGICAL CROSSOVERS

*Carl E. Moore and Bruno Jaselskis, Loyola University, Chicago*

Aside from the chemical balance, the pH meter (1) is probably the most widely used piece of chemical instrumentation and as such it has contributed much to both the progress and the culture of the hard sciences. This useful device came into being via an almost storybook route of discovery and development which culminated in the practical commercial Model G pH meter devised and marketed by an enterprising young college professor, A. O. Beckman. The flow of ideas, which climaxed in the development of this useful instrument, narrates one of the very interesting adventures in the sciences.

Beckman described this early venture into pH instrumentation in this manner (2):

.. in 1934, I experienced the type of luck in which preparedness played a role. I was then an assistant professor of Chemistry at California Institute of Technology. One of my University of Illinois classmates, Dr. Glen Joseph, .....happened to stop by one day for a chat. He told me of a serious problem he was having in making pectin and other by-products from lemon juice ... . He was forced to use a glass electrode, because it was not affected by  $\text{SO}_2$ . He used a thin-wall glass bulb about an inch in diameter, very fragile and easily broken. Furthermore, because the electric current used in measurements has to pass through the glass wall of the electrode, the extremely high resistance of the glass bulb (in the multimegohm range) forced him to use the highest sensitivity galvanometer available to serve as a null point in the Wheatstone bridge circuit employed for the voltage measurements.....

Professor Beckman suggested to his friend Dr. Joseph the use of a vacuum tube voltmeter which would allow him to use smaller and more sturdy glass electrodes than



A. O. Beckman, courtesy Beckman Instruments, Inc.

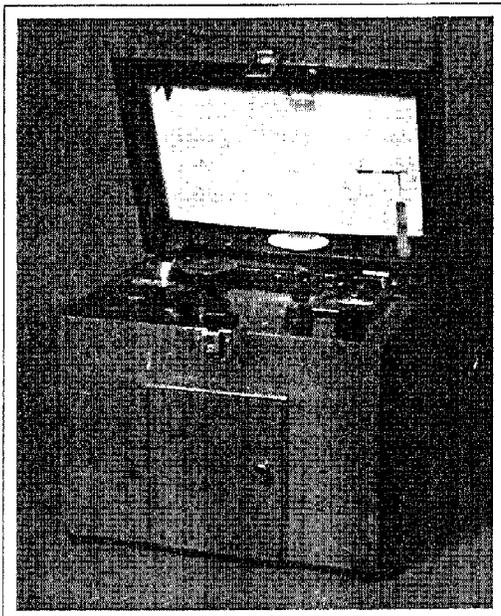
those electrodes that he had employed previously with the various unreliable and difficult to use electrometers. As a result of these discussions Beckman built a two-stage, directly coupled vacuum

tube voltmeter for Dr. Joseph. It luckily worked. In a few months his friend asked him to build him another instrument for his personal use. Then Beckman says:

The thought occurred to me — if he needed two of these instruments in his modest laboratory, perhaps other chemists might have a need for such an instrument.

In 1935 Beckman produced a portable rugged pH meter costing \$195 — a princely sum in those days and more than one month's salary for an analytical chemist. In this instrument the amplifier consisted of two vacuum tubes — a tetrode and a triode — and a milli-ammeter placed in

the plate circuit of the triode to serve as a balance indicator. As inconceivable as it may seem, this instrument, when introduced at the 1935 American Chemical Society Meeting in San Francisco, was



The Beckman pH meter

not received with enthusiasm. But some of the leading analytical chemists, though dubious about it, did suggest that he approach the instrument manufacturers and attempt to commercialize it. The instrument makers were generally pessimistic about this new fangled gadget. Beckman instead of letting the matter drop persevered and continued to make pH meters on his own, and in ten years he had made several hundred thousand, and there was no end in sight to the demand. As Beckman later pointed out, he was the right man in the right place at the right time: he had the correct training, foresight and energy to engineer a breakthrough in chemical instrumentation. It was of such mammoth proportions that only historians of a later time will be able to properly evaluate its impact.

But what set the stage for this monumental development? The answer to this question is couched in the romantic science of the electricians (3) which had captured the public imagination in the preceding century. Actually, as with nearly all things electrical, the pH meter can be said to have had its seminal origin in the work of Alessandro Volta, who announced on March 20, 1800 (4) the discovery of what we now call the Voltaic cell, which opened numerous paths of research. Each of these

operated nearly independently of the others, but occasionally these research paths would cross. These crossovers provided the opportunity for sharing vast amounts of an hitherto unknown technology by the investigators on each research path. This crossover phenomenon provided the impetus for many breakthroughs.

There are at least three intersecting courses of ideas — and their research tracks are easily discernible — in the discovery and development of the pH meter. These are

- the communications researchers' path of those researchers principally interested in improving the quality of telegraphic signals,
- the chemical research route of the investigators interested in acid-base chemistry, particularly in biological systems, and
- the physics research track into the study of the electrical properties of glasses.

All three of these lines of investigation were assiduously researched, each with its own specific sets of aims and objectives. However, none of these had goals that included the manufacture of a pH meter.

### The Chemical Research Pathway

By 1935 solution chemists — led by Ostwald's Leipzigers and their academic offspring — had elucidated much of the electrochemistry left over from the Faraday era. It was now possible to formulate and utilize Voltaic cells for a wide variety of purposes. Cells of the following general character were common knowledge.

| (Reference Electrode) || (Indicator Electrode) |

One of the applications of the cell was the determination of the concentration of redox substances.

These cells contained three elements:

- a reference electrode
- an indicating electrode and
- a device for measuring the voltage developed by the cell.

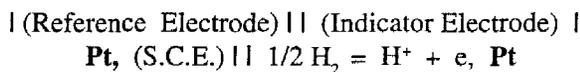
Each of these three cell elements offered many possibilities to experimenters in terms of materials used and devices constructed, and the history of each cell component in itself is a monument to the ingenuity of the early experimenters.

By the time of Beckman, the calomel electrode and its attendant salt bridge, both of which had been developed in Ostwald's laboratory, had been generally accepted as the half cell device most practical for the standard of reference. But there still remained substantial

problems facing workers in the decade of the 1930s in terms of the discovery and fabrication of practical indicating electrodes and in the development of suitable voltage measuring devices.

An indicating electrode for the ubiquitous hydrogen-ion posed some very special and difficult problems in that the hydrogen-ion occurred in all aqueous solutions, and many of these solutions both *in vivo* and *in vitro* contained materials which were deleterious to the usual hydrogen-ion sensing electrodes rendering them useless. However, of the many electrodes studied, two indicating electrodes — the hydrogen electrode and the glass electrode — played the most significant roles in the development of the pH meter. The glass electrode eventually became the electrode of choice for almost all pH measurements.

The pH measuring cell employing the hydrogen electrode may be formulated as follows:



In the case of the hydrogen electrode, which depended on a catalytic platinized-platinum metal surface, there were two major difficulties. First, the electrode became easily "poisoned" in the catalytic sense — its surface was easily contaminated by many things, particularly organic compounds containing sulfur, rendering the electrode erratic or inoperative — and second, the hydrogen electrode was easily polarized if current was drawn from the cell. Thus the use of devices employing bridge circuits required significant amounts of time for each measurement in order to allow the circuit to reestablish equilibrium. This behavior made the hydrogen electrode difficult to use in potentiometric titrations of acids and bases.

### The Communications Pathway

There had been intense activity in the communications area following the discovery that telegraphic signals could be sent by wire. It was soon found that telegraphic signals needed power boosts if they were to travel long distances. Thus a research pathway opened up which produced efficient test instrumentation and signal booster devices. Some of this equipment was, with appropriate modification, adaptable to other fields. In the course of this intensive communications research Fleming (1905) discovered the thermionic diode (5). Two years later — still on the communications path — Lee de Forest discovered the triode (6) which was to make Beckman's pH meter possible. The spirit of the

times is captured in de Forest's account of his discovery of the triode to which he gave the name "Audion (6)":

... The "Audion," suggestive of sound, prompts the consideration of an analogy in the realm of sight — the microscope. The Audion, in a measure, is to the sense of sound what the microscope is to that of sight. As the microscope has opened to man new worlds of revelation, studies of structure and life, and manifestations of natural processes and chemical reactions whose knowledge has proven of inestimable value through the past three generations, so history, opened fields of research and wrought lines of useful achievement which may not unfairly be compared with the benefits from that older prototype and magnifier of light waves. But when the first steps were taken in the work which eventually resulted in the Audion of today, I no more foresaw the future possibilities than did the ancient who first observed magnification through a drop of water.

In 1900, while experimenting with an electrolytic detector for wireless signals, it was my luck to be working by the light of a Welsbach burner. That light dimmed and brightened again as my little spark transmitter was operated. The elation over this startling discovery outlasted my disappointment when I proved that the unusual effect observed was merely acoustic and not electromagnetic. The illusion had served its purpose. I had become convinced that in gases enveloping an incandescent electrode resided latent forces which could be utilized in a detector of Hertzian oscillations far more delicate and sensitive than any known form of detecting device. The first "commercial" Audion, as it originally appeared in 1906, was therefore no accident or sudden inspiration.

The advent of the triode opened up a wide area of applications other than in the field of communications. The first application of the triode to hydrogen-ion chemistry (7) appears to be that of Kenneth H. Goode, who carried out a Master of Science degree research project at the University of Chicago. This research involved using the triode in a potentiometric titration setup. The MS degree was granted in August of 1924, but Goode published a paper on the research in 1922. (8) The research was so close to the frontier of the science of the time that this paper contains no references to previous work. He performed the titrations using a hydrogen electrode versus a calomel electrode, with his continuous reading apparatus giving the readout in either volts or Sorensen units, *i.e.*, pH units. Goode gives his reasons for doing the research as follows (7):

...In order to avoid the use of the telescope and scale, which do not lend themselves to convenient use ei-

ther for classroom demonstrations or for routine titration work, it occurred to the writer to make use of the amplifying characteristics of the vacuum tube to magnify the currents to such a value that they could be easily measured with a portable milli-ammeter. . .

Goode in his paper in the *Journal of the American Chemical Society* made the fundamental observation that, because of his use of the triode, his device drew no current. This observation was seminal to its use with the glass electrode which was to follow some seven years later (8):

... The simplest possible apparatus for electrometric titration, from a theoretical standpoint, would be a sensitive voltmeter connected between a calomel electrode and a hydrogen electrode. In practice, however, an ordinary voltmeter cannot be used, because the instrument would consume current enough from the cell to discharge the hydrogen electrode, and render it inoperative. For this reason all types of apparatus hitherto in use have depended upon balancing the unknown e.m.f. of the cell being used against a variable known e.m.f. produced by a potentiometer system, the balance being determined by a "null-point" galvanometer. With this type of apparatus a balance of potentials must be made before each reading of the voltage, and there is considerable uncertainty in the readings when the potential of the cell is rapidly changing. The investigation described in this paper has shown that the 3-electrode vacuum valve ("audion") presents almost the ideal case of a "voltmeter" which draws no current from the source to be measured, and can therefore be employed as a continuous-reading instrument for determining the concentration of the hydrogen ion. ...

### The Physics Pathway

The electrical properties of glasses which started to attract attention at around the time of the development of the Leyden jar in the 1740s, developed into a major research area. Many famous names are associated with this research pathway. Among these we mention Benjamin Franklin, Lord Charles Cavendish, Lord Kelvin, Helmholtz, Warburg, Cremer, and Haber. Undoubtedly, many frustrating hours, days, perhaps even years were spent in trying to overcome the problems posed by the very high electrical resistance of glass. The glass research pathway intersected both the communications track because of the need for effective insulators and the main stream of solution chemistry because of its possibilities for indicating electrodes for the hydrogen-ion. At these intercepts the fruits of a vast amount of high quality research became available to the pH in-

strument constructors and the communications researchers.

After a surprising lull of around seven years following the publication of Goode's paper, at least three laboratories almost simultaneously developed pH-measuring devices based on the use of the glass electrode. These were Partridge at New York University, Elder and Wright at the University of Illinois, and Stacie and Goodhue at Iowa State College. The first paper to appear in print was that of Elder and Wright (9). We will



Walter H. Wright holding 199 Tube used for glass electrode measurements (1928), (see Ref. 12)

consider the paper of Elder and Wright in some detail, not only because of their established priority, but also because of the fact that, at the time of this literature study, Walter Wright was still alive—albeit in a nursing home—and could provide some very interesting anecdotal information. It was our very good fortune (10) to make contact with Wright (born October 23, 1907), the surviving author of the paper which had appeared in the *Proceeding of the National Academy of Sciences* in 1928. He was kind enough to give us a personal account of his recollections of that research. In this account he indicated that the germ of the idea came from a course entitled Advanced Analytical Instruments which was being taught at the University of Illinois by Dr. Lucius W. Elder, Jr. There was much discussion of pH determination in that class of methods, but Mr. Wright was not

sure who suggested the idea of using a vacuum tube potentiometer with the glass electrode to improve its usefulness as a pH sensing device. Thus, we will probably never know the identity of "the one of us" to whom the paper refers in the quote "...it occurred to one of us that a vacuum tube potentiometer might be preferable."

Under the direction of Elder, Wright did honors undergraduate research and an honors undergraduate thesis (11), which addressed the problem of utilizing a VTVM with the glass electrode. At the time of this summer school class, Mr. Wright, who had a previous interest in radio and electronics dating back to the days of World War I, had built a functioning one-tube radio receiver. Thus, he was well suited for the task of constructing a functioning vacuum tube voltmeter. He was faced with the dual and formidable problems of constructing both a vacuum tube voltmeter and a glass electrode. It is interesting to note from his correspondence that he cannibalized his one-tube radio receiver to get parts for the construction of his VTVM. The essence of these memories is given in the letter on the following page(12):

Three major research pathways — the turbulent torrent of solution chemistry, the difficult trail of the physics of the electrical properties of glass, and the raucous road of communications research — converged. At the convergence point, these combined pathways provided science the information and technology needed to allow skilled hands and creative minds to fabricate the pH meter, an instrument that has impacted on much of succeeding research. The Model G pH Meter of A. O. Beckman was the practical manifestation of these research efforts.

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7. K. H. Goode, Continuous Reading Electrotitration Apparatus, M.S. Thesis, University of Chicago, 1924.
8. K. H. Goode, "A Continuous Reading Electrotitration Apparatus;" *J. Am. Chem. Soc.*, **1922**, 44, 26.
9. L. W. Elder and W. H. Wright, "pH Measurement with the Glass Electrode and Vacuum Tube Potentiometer," *Proc. Natl. Acad. Sci. USA*, **1928**, 14, 936-939.
10. We owe thanks to the late Prof. John C. Bailar, Jr. of the University of Illinois at Champaign/Urbana, who assisted us in locating Mr. Wright.
11. W. H. Wright, pH Measurement with the Glass Electrode and the Vacuum Tube Potentiometer, B.S. Thesis, University of Illinois, 1929.
12. Letter from W. H. Wright to C. E. Moore, Nov. 7, 1985. It was welcome news to find that the original vacuum tube used in the first VTVM pH meter was still in his possession. The photograph of Wright and his vacuum tube is in the Loyola University Archives in the Moore correspondence. Wright's recollections of the details of this research —nearly 60 years later—are contained in his correspondence with Moore.
13. Some of the early pH sensing electrodes such as quinhydrone contaminated the samples.
14. W. H. Wright died in April, 1990.

## ABOUT THE AUTHORS

Professors Moore and Jaselskis are professors of chemistry emeritus at Loyola University Chicago, 6525 N. Sheridan Road, Chicago, IL 60626. Both are considered generalists in the field of analytical chemistry. Jaselskis has worked extensively in the field of solution chemistry and Moore in the domain of organic reagents.

Wilmington, DE 19809  
November 7, 1985

Dear Professor Moore:

At the University of Illinois (Urbana) Summer Session in 1928 I was taking a course in Advanced Analytical Instruments under L. W. Elder, Jr. pH instruments were then possible contaminants [(13)] of the sample being examined except for the glass electrode. However, the glass electrode required a quadrant electrometer to avoid polarizing the glass electrode such as when ordinary Wheatstone bridge type instruments were used. Unfortunately, low humidity is essential for accurate readings with quadrant electrometers particularly during a humid summer at U. of Ill.

Goode's proposal (1921) to use a 3 electrode vacuum tube failed to recognize the basic space charge and ion or electron flow factors of the triode. My experience with wireless and radio dating back to World War I gave me electronic training.

For a bachelor degree thesis I proposed a vacuum tube potentiometer with grid voltage set at a value where no current flow in the grid circuit would take place. I dismantled my one tube (UV199) radio set and proceeded to set up the apparatus used in the paper published in the 1928 proceedings N. A. S. pg. 936.

The first attempt at pure soda-lime glass preparation was a disaster! The melt was made in a platinum dish and heated in a 20KW carbon granule furnace equipped with a tap-off transformer and protected by a circuit breaker in the power supply. I had been assured that the furnace would not melt Ferro-Silicon (approx. 1590° C) and was therefore safe for platinum (M.P. 1753° C). I reasoned that furnace power supply maximum could be 20KW so I set the tap-off transformer at the highest voltage to keep under this figure. When the breaker tripped I set the tap-off transformer at the next lower tap, reset the breaker and repeated the process. As the furnace temperature rose, the carbon resistance fell, thus drawing more current and tripping the breaker. I followed the temperature rise by observing a range of segar cones placed alongside the platinum dish. After several cycles of above steps I removed the lid to observe the melt. White light came from the furnace, the segar cones had melted, also the platinum dish and its charge! One explanation was that the platinum dish (\$300 worth) had been purchased during World War I and therefore might not be pure platinum. I then looked up the thesis (CA 1915) covering the original use of the furnace for preparation of Illium type alloys for S. W. Parr. The original user apparently was afraid to trip the breaker and thus never the full 20KW available and hence did not reach the temperature possible. In any event the contents of the furnace bottom was removed and turned over to an inorganic grad student (S.G.Ford) for platinum recovery. The next move was to use a graphite crucible and risk some impurity in the glass being picked up from the binder used in the crucible. The melt from the graphite crucible did have a slight purple cover possibly due to manganese or cobalt(?). Finally, a large Nickel crucible was used resulting in a melt that was drawn into small rods with a slight brown color, probably due to a trace of dissolved nickel oxide.

As Dole pointed out in his book several workers were in this field at the same time. It just so happened that the novelty of the Elder & Wright study led to early publication in the Proceedings of the National Academy of Science 14, 936 - 9 (1928) and thus predated the publications of the other workers.

The first inquiry following publication was from Dr. Ellice McDonald of the Cancer Research Fund, Graduate School of Medicine, University of Pennsylvania Philadelphia, PA.

His interest related to the possibility that Cancer cells differed in pH from normal cells and that the glass electrode could possibly detect the difference

Sincerely yours,

Walter H. Wright (14)

P.S. I still have the 199 tube and some of the soft glass tubing used in this study.