Guest Forum

The Screening Committee Lecture for the First Dr. Masao Horiba's Award

pH Measurement using the Harned Cell

-pH Values Acceptable for the International Society-

Susumu Nakamura
National Institute of Advanced Industrial Science and Technology (AIST),
National Metrology Institute of Japan (NMIJ),
Inorganic Analytical Chemistry Division,
Senior Research Scientist
Doctor (Engineering)

The internationally agreed method of measuring pH values is using the Harned Cell. In Japan, pH measurement using the Harned Cell is performed at the National Metrology Institute of Japan (NMIJ) of the National Institute of Advanced Industrial Science and Technology (AIST). Japan can supply pH values based on the international comparison of measured values.

International Traceability System

All over the world, standards of measured length and mass are identical, however standards of pH values are subtly different. The traceability for international pH values has not yet been established. The definition of measurable pH values differs in each country. According to ISO Guide 30[*1], traceability is defined as “the characteristics of the values of measured results or the standards normally related to the National Standard or International Standard, through a chain of comparison without break in which all uncertainty is expressed.” It is important who is finally responsible for that value.

In the physical standards system, there is an international standard called the Primary Standard defined in SI units. Furthermore, a Secondary Standard and Working Standard are prepared under Primary standard, and the country responsibly presents these standards to the user. In addition, traceability is required for the transitions of Primary Standard → Secondary Standard → Working Standard.

On the other hand, the chemical standards system is used with reference materials instead of the SI units defined by the primary standard. Figure 1 shows the difference between the traceability systems of the physical and chemical standards systems.

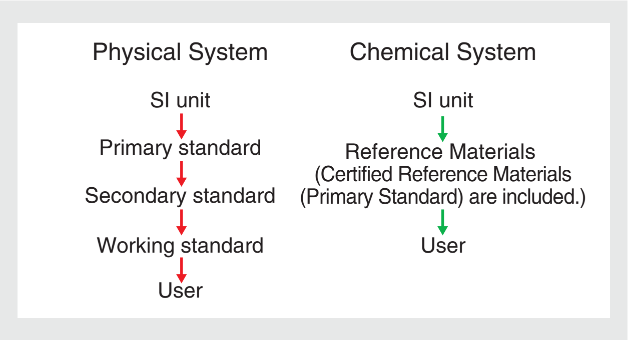

Figure 1 Traceability System for Physical and Chemical Standards

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*1: “Term and definitions used in connection with reference materials.”

According to ISO Guide 30, reference materials are defined as “Materials or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.” The properly determined Reference Materials with a certificate are called Certified Reference Materials (CRMs). These materials are defined as “Reference materials, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty level of confidence (ISO Guide 30).”

International Standardization Organization

The following four organizations of chemistry may be considered to produce Certified Reference Materials. However, only the CIPM[*2](International Committee of Metrology) can be responsible for the values of Certified Reference Materials. Because the research institute of the country that constitutes the CIPM is responsible for the values of Certified Reference Materials.

1. CIPM
2. ISO (International Organization for Standardization)
3. IUPAC (International Union of Pure and Applied Chemistry)
4. OIML[*3] (International Organization for Metrology Legal)

For reference, 1.NMIJ/AIST, 2.JIS (Japanese Industrial Standards), 3.CSJ (Chemical Society of Japan), and 4.JIS correspond to above organizations of 1 to 4 respectively.

*2: Comité International des Poids et Mesures.

*3: Organisation Internationale de Metrologie Legale.

Constitution of the CIPM (International Committee of Metrology)

The CIPM is working under the “Convention of Meter” and it is advancing, focusing on every area of activity all over the world. The CIPM’s position is at the top of the hierarchy and is concerned with overall coverage of the area committees. For example, the CCL[*4] is the consultation body concerned with length, the CCT[*5] with temperature, and the CCQM[*6] (Consultative Committee for Amount of Substance) with the establishment of chemical standards. They are established as direct subordinates of the CIPM. Other technical committees similar to the CCL, CCT, and CCQM are also established and working in each of the above areas.

*4: Comité Consultatif des Longueurs.

*5: Comité Consultatif de Thermométrie.

*6: Comité Consultatif pour la Quantité de Matière.

The CIPM Certification Method

In the CIPM, Primary Standards should be mutually consented and certified among countries. The certification consists of a document and Appendices A, B, and C. Appendix A is the list of national metrology institutes concerned with the establishment of the standard. Appendix B is a list of capabilities of each institute. Appendix C is a list of materials or substances certified by national metrology institutes.

In Appendix C, the relationships between the CRM, CMC[*7], etc., are defined as the following:

1. All CRMs are primary standards.
2. CRMs are certified by CMCs.
3. CMCs are certified by Key Comparison and a peer review.

*7: Calibration and Measurement Capability.

“Key Comparison” means the mutual comparison of the unknown samples measured in research institutes in two or more countries. “Peer review” means a confirmation of measuring capability by specialists. “Key Comparison” and “Peer review” certify the calibration and measurement capability of each research institute. For that, the general requirements of ISO17025*8 has to be satisfied. Furthermore, those research institutes are providing CRMs as the Primary Standard according to ISO Guide 34*9.

Measuring the pH Value

pH is one of the most important parameters of aqueous solutions. By notional definition pH is defined as the relative activity of hydrogen ions in solution:

$$pH = -\lg a_{H+} = -\lg(m_H \gamma_H / m^0),$$

where a_{H+} is the relative activity and γ_H is the molal activity coefficient of the hydrogen ion H^+ at the molality m_H, and m^0 is the standard molality.

Since a single ion quantity cannot be determinable by any thermodynamically valid method, an instrumental definition of pH is based on an electrochemical cell without transference using the hydrogen gas electrode, known as the Harned Cell.

A conventional procedure developed at NBS[1] and recommended at present by the last IUPAC Recommendations[2] is used in most of the NMIJ for assignment of pH values to primary pH standard buffer solutions.

The NIST in the U.S. and PTB*10 in Germany have presented pH values using the Harned Cell method. In Japan, the pH values in JIS Z 8802 (Methods for Determination of pH of Aqueous Solutions) are not accepted in the international society. For, the values are based on OIML 1980 recommendation in which the Harned Cell is not used.

Harned Cell Method

pH measurement using the Harned Cell is carried out by measuring the potential difference of the cell I (Harned Cell), containing certified standard buffer solution and chloride ions, added in order to use the silver-silver chloride electrode:

$$\text{Pt} \mid H_2 \mid \text{buffer solution, } Cl^- \mid AgCl \mid Ag \text{ .... Cell I}$$

The potential difference E of this cell (corrected to 101.325 kPa partial pressure of hydrogen) is described by the following equation:

$$E = E^0 - \frac{RT \ln 10}{F} \lg\left(\frac{a_H m_{Cl} \gamma_{Cl}}{m^0}\right) \text{ .... (1)}$$

which can be rearranged to give the acidity function:

$$p(a_H \gamma_{Cl}) = -\lg(a_H \gamma_{Cl}) = \frac{E - E^0}{(RT/F)\ln 10} + \lg\left(\frac{m_{Cl}}{m^0}\right), \text{ .... (2)}$$

where E^0 is the standard potential difference of the cell, γ_{Cl} is the molal activity coefficient of the chloride ions at the molality m_{Cl}, R-the universal gas constant, F-the Faraday constant and T-thermodynamic temperature.

A pH primary procedure consists of the following steps.

1) Measurement of the standard potential difference E^0

   E^0 is determined from potential difference $\overline{E}$ of Harned Cell filled with hydrochloric acid at molality m_{HCl} (~0.01 mol·kg^{-1}), accordingly to equation:

   $$E^0 = \overline{E} + \frac{2RT \ln 10}{F} \lg\left(\frac{m_{HCl} \gamma_{\pm HCl}}{m^0}\right), \text{ .... (3)}$$

   using mean ionic activity coefficient of HCl $\gamma_{\pm HCl}$.

   To find accurately m_{HCl} the NMIJ uses a coulometric titration of hydrogen ions (horizontal 3-compartment cell, constant current 50 mA) with endpoint detection by combined glass electrode.

2) Determination of acidity function

   Acidity function values of buffer solution are determined at 0.005, 0.010, 0.015 and 0.020 mol·kg^{-1} of chloride ions. NaCl, used to provide Cl^- certified solutions beforehand dried during 2 hours at 450 °C.

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*8: General requirements for the competence of testing and laboratories.

*9: Quality system guidelines for the production of reference materials.

*10: Physikalisch-Technische Bundesanstalt.

3) Extrapolation of the acidity function to zero chloride molality

The acidity function value at zero chloride molality $pa_0 = -\lg(a_H \gamma_{Cl})_{m_{Cl\to 0}}$ is determined by linear extrapolation of the acidity function values obtained in step 2 by Least Square Method (Figure 2).

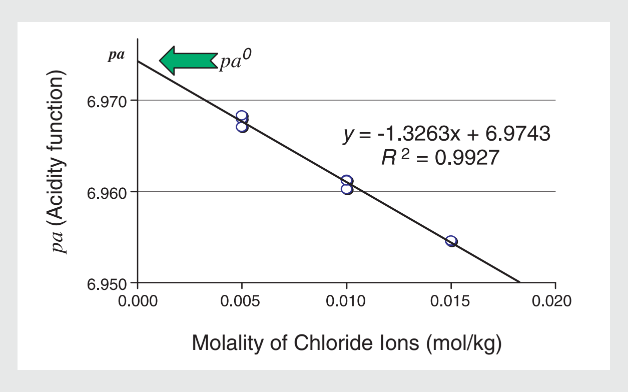

Figure 2 Chloride Ion Concentration and ***Pa*** (Extrapolation to Zero Chloride Ion Concentration)

4) Calculation of trace activity coefficient of chloride ions $\gamma_{Cl\to 0}$ at $m_{Cl\to 0}$ at According the Bates-Guggenheim convention[*11] [3]:

$$\log \gamma_{Cl\to 0} = -\frac{AI^{1/2}}{1 + 1.5 \cdot I^{1/2}} \; , \; \ldots\ldots\ldots\ldots \; (4)$$

where A is the Debye-Hückel temperature-dependent limiting slope[3] and I the ionic strength of the buffer solution. If ion molar concentration is C_i, number of electric charges is Z_i; $I = (1/2)\,\Sigma\, C_i Z_i^2$.

[*11] Specific numerical value (1.5) is substituted for the coefficient of a Debye-Hückel diffusion equation.

5) Calculation of pH

pH value of standard solution is obtained according to following equation:

$$pH = pa_0 + \lg \gamma_{Cl\to 0} \; \ldots\ldots\ldots\ldots \; (5)$$

Harned Cell of the National Institute of Advanced Industrial Science and Technology (AIST)

The Harned Cell of AIST is shown in Figure 3.

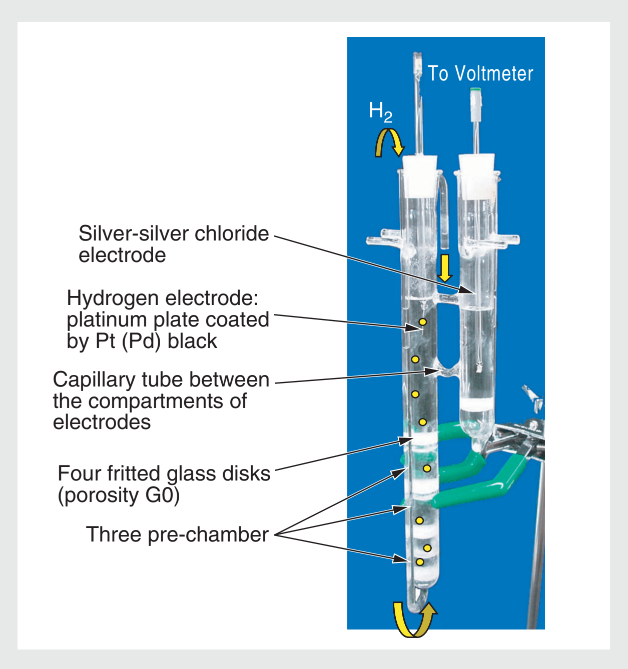

Figure 3 The Harned Cell of the National Institute of Advanced Industrial Science and Technology

The Harned Cell has 5 compartments; one of hydrogen electrode, one of reference electrode (both are connected by capillary tube) and three pre-chambers with 4 fritted glass disks designed to saturate hydrogen gas by water vapor and reach needed temperature. By this tube gas enters the cell. The flow rate is 4 to 10 mL/min. Diameter of bubbles was approximately 1 mm. Stabilization time for the experiment was about 3 hours.

The pH measuring system currently used is shown in Figure 4.

The system consists of 6 Harned Cells immersed in a water thermostat bath. We measure EMFs for cells by a voltmeter and check atmospheric pressure and temperature. The whole system is overseen by the computer.

The data were recorded each 5 min over 24 hours. The pH measurement is performed with a temperature control tolerance of ±0.005 K inside the thermostat bath.

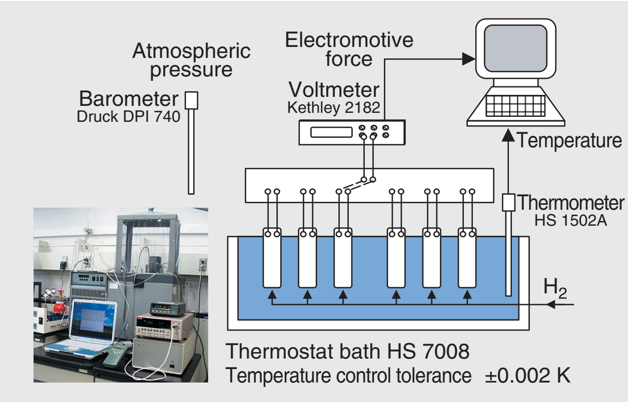

Figure 4 Measuring System

Experimental Results using the Harned Cell

- Example of electromotive force measurement

As an example of electromotive force measurement, in Figure 5, measured values are plotted with intervals of 5 minutes. It takes approximately three hours to make the value stable, then the stable condition continues at 20 µV for twenty hours.

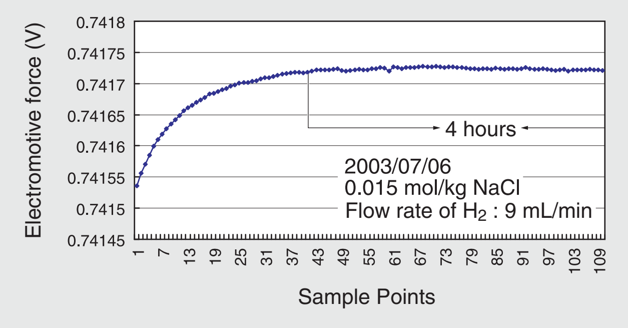

Figure 5 Example of Electromotive Force Measurement of the Harned Cell in AIST

- Standard potential of silver-silver chloride electrode

In CCQM, it has been agreed that the standard potential of a silver-silver chloride electrode will be used within the range of 222.464 ±0.1 mV at 25 °C. Six silver-silver chloride electrodes with close standard potentials were selected for six cells at the same time. The values were E^0=222.477 ±0.027 mV.

- pH value of buffer solutions

The pH values of buffer solutions of Phosphate[*12], Phthalate[*13], Oxalate[*14], Borate[*15] were measured at 15 °C, 25 °C, and 37 °C so as to be compared with the PTB data in Germany[4]. Only the data of the Phosphate is shown (Table 1) here. All pH values and uncertainties of buffer solutions are very similar to those of the PTB. AIST will have standard pH values in Japan and so the registration has been applied for [Appendix C] (February, 2005).

*12: At 25 °C: pH 6.865.

*13: At 25 °C: pH 4.007.

*14: At 25 °C: pH 1.681.

*15: At 25 °C: pH 9.184.

Table 1 pH Values of Phosphate Buffer Solution

Temperature	pH (NMIJ/AIST)	pH (PTB)	ΔpH
15.000 °C	$6.899_7 \pm 0.002_2$	6.900 ±0.002	0.000_3
25.000 °C	$6.865_4 \pm 0.002_2$	6.865 ±0.002	0.000_4
37.000 °C	$6.840_7 \pm 0.002_4$	6.841 ±0.002	0.000_3

Conclusion

pH is one of the most important parameters of aqueous solutions. Every country has very strict pH parameters for drinking water, wastewater, etc. However, a very high level of technical know-how is required for pH measurement.

This field forms a large global market, but there are a few countries that can provide the Reference Materials to the market. Japan is a country that can supply the standard of the pH values using the Harned Cell. There are many countries that cannot measure pH values using the Harned Cell. To such countries, Japan can offer a pH standard as a Primary Standard.

Reference

[1] Richard A. Durst, Standard Reference Materials: Standardization of pH Measurements, National Bureau of Standards Special Publication 260-53, October (1975).

[2] Buck R.P., Rondinini S., Baucke F.G.K., Camoes M.F., Covington A.K, Milton M.J.T., Mussini T., Naumann R., Pratt K.W., Spitzer P., Wilson G.S., The Measurement of pH - Definition, Standards and Procedures, Report of the Working Party on pH, *Pure and Applied Chem.*, Recommendation (2002).

[3] Bates R. G., Guggenheim E., *Pure and Applied Chem.*, **1**, 163-168 (1960).

[4] Bilateral comparison between NMIJ, Japan and PTB, Germany. pH determination of primary reference buffer solutions by Harned cell measurements. Final Report, Susumu Nakamura (NMIJ), Igor Maksimov (NMIJ), Petra Spitzer (PTB), Janine Giera (PTB).

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