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PH TRACEABILITY SYSTEM IN JAPAN

The pH primary method was developed at NMIJ in order to support Japanese field-laboratories to meet currently intensified requirements. The outline of the pH traceability system in Japan is described.

Keywords: pH measurement, pH uncertainty, buffer solution, Harned cell, traceability chain.

Present-day pH definition Until recently, the main guideline for pH measurements was set out by the IUPAC Recommendations of 1984 [1]. The serious metrological deficiencies of this paper were discussed broadly [2], e.g. the coexistence of two pH scales in violation of basic principle of uniformity of measurements. The pH values of standard buffer solutions were considered as some fixed reference points for one of two scales and presented as a “mean of a large number of determinations...”.

The new IUPAC Recommendations [3] published in 2002 endorse only the original definition of pH as the negative logarithm of the hydrogen ion activity. This document recognizes, as a primary method for measurement of pH, only an electrochemical cell without transference (Harned cell). Such an approach leaves no place for “any pH scale” and gives the hierarchical system of pH measurements.

The new IUPAC Recommendations were officially backed [4] by the Electrochemical Analysis Working Group (EAWG) of the Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM), BIPM.

Development of Japan Calibration Service System (JCSS) for pH measurements Previously the JCSS for pH was stemmed from six primary pH solutions similar to those of the set of recently cancelled Japanese Industrial Standards JIS K 0018 - JIS K 0023. This group of JISs was ideologically based on the OIML International Recommendation R54 [5]. From a metrological point of view, the last document is more consistent than Ref. [1], but it relies heavily upon the purity of original chemical reagents used to prepare the primary buffer solutions. In the spirit of R54, the National Metrology Institute of Japan (NMIJ) checked the purity of the reagents in order to secure that the amounts of impurities in initial solutes are less than or equal to those in the NIST CRMs [6]. Thereupon six kinds of primary buffer solutions were prepared and distributed with an ascribed pH expanded uncertainty 0,005 (coverage factor $k = 2,95\%$ confidence interval).

According to the new IUPAC Recommendations, the “batch-to-batch variations in purity can result in changes in the pH value of samples of at most 0.003” for primary solutions. Therefore, the stipulation of R54

about “an error not exceeding $\pm 0,01$ pH unit” looks very reasonable for the past. Nevertheless, modern studies, e.g. in biochemistry or pharmacology, ask for more precise buffers with pH uncertainty 0,003 or better. And, in consideration of the GUM [7], as any result of measurement, a certified pH value should be reported with the value of its experimental uncertainty.

Therefore, in the last decade the JCSS for pH is being modernized to fulfill nowadays requirements.

Development of Harned cell in Japan and confirmation of NMIJ CMCs. The detailed description of the NMIJ pH measurement set-up based on the Harned cell is given in Ref. [8].

According to a BIPM pilot study [9] the main contribution to pH uncertainty is given by concentration measurement of dilute hydrochloric acid used afterwards to determine the standard potentials of reference electrodes. Such contribution can contribute to as much as 60% to 80% of the standard potential uncertainty, i.e. to be of vital importance for pH precision. NMIJ was capable to reach the expanded uncertainty $5 \cdot 10^{-6}$ mol/kg or 0,0006 in term of pH for coulometric titration of acid. Such small concentration uncertainty decreased the contribution of this parameter to $\sim 30\%$. Consequently, the other factor, the uncertainty of the electromotive force measurement, became more significant. In order to deal with it, NMIJ undertook a three-year study for stability of standard potentials of reference electrodes. Although some recent publications [10, 11] suggest that the maximal time to use silver-silver chloride electrodes of thermal-electrolytic type is about 200 days, the long-term stability study showed that appropriate fabrication and handling ensured the normal electrodes' functioning for at least 2 years. Within this period a fairly small aging potential degradation of $40 \mu\text{V}$ was observed and the expanded uncertainty of standard potential for reference electrodes was estimated $\sim 35 \mu\text{V}$ or 0.0006 in term of pH.

The above-mentioned improvements allowed NMIJ to attain the pH expanded uncertainty 0,003 for primary buffers. This estimation was successfully confirmed during the cycle of CCQM key comparisons for pH (CCQM-K9.2, K18, K19, K20) [12].

In addition to a widespread classic type of Harned cell, NMIJ developed another design of cell for instable solutions, mainly that of the carbonate buffer [13].

NMIJ pH primary solutions A few years ago, the EAWG held the discussion on the subject of the best way to supply the pH CRMs. The new IUPAC Recommendations describe how to produce the primary standard buffer by means of Harned cell, but give no indication about its subsequent distribution. Traditionally, for many decades NMIs supply the solid-based CRMs, with the advantage of long lifetimes. NMIJ recently measured the pH values of solutions made from 30-year-old NIST CRMs and all the determined pH values were in good agreement (within the declared expanded uncertainty 0,005) with ones on the certificates. This approach is used by NIST, PTB, OIML and VNIIFTRI.

However, for such CRMs the customer is expected to exercise a certain level of skill to correctly store the reagent, to make appropriate operations (crushing, drying etc.) and finally to prepare by himself the primary buffer from the solid. Additionally, not everyone has access to high-purity deionized water – such as the product of the Millipore Purification System – that is needed for preparing buffers.

NMIJ (as, for example, SMU) prefers to supply liquid-based buffers, ready-to-use for any customer just after opening the bottle. The main problem for such CRMs, the carbon dioxide contamination of alkaline solutions from atmospheric air, was resolved by the sealing of a HDPE bottle with buffer in an aluminium foil bag. The monitoring showed an insignificant decrease of the pH (of order of 0,001) for both borate and carbonate buffers in such bags during one year.

At present, NMIJ produces and supplies six kinds of buffers in the pH range from 1 to 10: 0,05 m (mol/kg of solvent) potassium tetraoxalate, 0,05 m potassium hydrogen phthalate, 0,025 m Na_2HPO_4 + 0,025 m KH_2PO_4 , 0,03043 m Na_2HPO_4 + 0,008695 m KH_2PO_4 , 0,01 m disodium tetraborate and 0,025 m NaHCO_3 + 0,025 m Na_2CO_3 solutions. The expanded uncertainties of pH values determined at three temperatures (15 °C, 25 °C and 37 °C) do not exceed 0,004. According to ISO Guide 34 all NMIJ pH CRMs have an expiry date stated on the certificates. The validity period of certificate is, in principle, six months after the measurement date, but it has to be covered by one year guarantee afterward the initial solution preparation date.

Outline of JCSS for pH measurements in the future For the time being, the primary pH method with the expanded uncertainty $\sim 0,003$ (in the term of conventional meaning of pH, see Fig.1) is maintained at NMIJ. If necessary, the traceability of the pH value to the SI could be established with the expanded uncertainty $\sim 0,01$, taking into account the uncertainty of the Bates – Guggenheim convention [14].

The primary buffers provided by NMIJ serve to calibrate the secondary solutions by a conventional glass-electrode method in the designated calibration body, Chemicals Evaluation and Research Institute (CERI). For the sake of the highest precision, each secondary pH solution is derived from the primary one of the same nominal chemical composition. The pH uncertainties of the secondary buffers at present are under discussion.

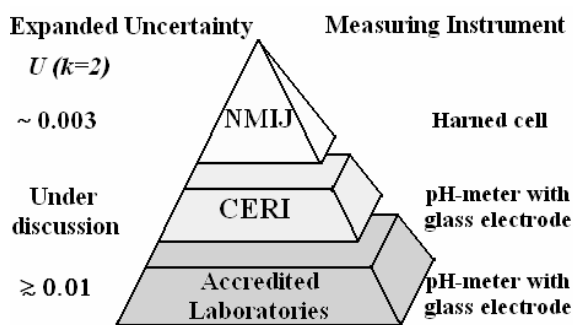


Fig. 1. JCSS traceability chain on pH measurements

Finally, CERI is responsible for the transference of pH unit to the accredited laboratories. At the moment, those for commercial pH buffers under the JCSS are: Junsei Chemical Co., Ltd.; Kanto Chemical Co., Inc.; Katayama Chemical Industries Co., Ltd.; Kishida Chemical Co., Ltd.; Nacalai Tesque Inc. and Wako Pure Chemical Industries, Ltd.

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ЗАБЕЗПЕЧЕННЯ ЄДНОСТІ pH-ВИМІРЮВАНЬ В ЯПОНІЇ

І. Максимов, М. Охата, А. Хіюкі, К. Чіба

Основні методи pH-вимірювань були розроблені в Національному японському метрологічному інституті для забезпечення роботи японських лабораторій в умовах вимог, що посилюються, до них. У статті наведена розробка японської системи калібрування для pH-вимірювань і розробка елемента Харнеда, схваленого Національним японським метрологічним інститутом. Також описано забезпечення єдності pH-вимірювань в Японії.

Ключові слова: pH-вимірювання, pH-невизначеність, буферний розчин, елемент Харнеда, система забезпечення єдності вимірювань.

ОБЕСПЕЧЕНИЕ ЕДИНСТВА pH-ИЗМЕРЕНИЙ В ЯПОНИИ

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Основные методы pH-измерений были разработаны в Национальном японском метрологическом институте для обеспечения работы японских лабораторий в условиях ужесточающихся требований к ним. В статье приведена разработка японской системы калибровки для pH-измерений и разработка элемента Харнеда, одобренного Национальным японским метрологическим институтом. Также описано обеспечение единства pH-измерений в Японии.

Ключевые слова: pH-измерение, pH-неопределенность, буферный раствор, элемент Харнеда, система обеспечения единства измерений.