Establishment of Traceability Chain For pH Measurement in Indonesia

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Abstract. As a consequence of the globalization of trade and industries, the presence of an accurate and traceable measurement has become very important for quality assurance of a product or service in the market, including pH measurement. pH measurement is a basic analysis used in a wide variety of applications, such as agriculture, wastewater treatment, industrial processes, research and development, and environmental monitoring. The reliable and comparable results of pH measurement are advantaged as one of the parameters for quality control that will affect the decision making. The Electrochemistry Laboratory under Deputy of National Measurement Standard – National Standardization Agency of Indonesia (SNSU–BSN) has a main duty to ensure the reliability, comparability, and traceability of pH measurements in Indonesia, as a commitment in building chemical metrology infrastructure. In this article, all the activities related to the establishment of traceability chain for pH measurement in Indonesia are comprehensively discussed. As of currently, the Electrochemistry Laboratory has successfully developed the secondary method for pH measurement using differential potentiometric cell, production of certified reference material (CRM) for buffer solution (oxalate, phthalate, phosphate, and borate buffer), dissemination by proficiency testing (PT) schemes for pH measurement, participation in the key comparison (KC) of APMP.QM-K91 for phthalate buffer, and claim submission for the Calibration Measurement Capabilities (CMCs) of phthalate buffer (pH 3.97-4.03) with expanded uncertainty 0.004.

1. Introduction

The viable globalization of trade and the complex manufacturing in recent years has caused a significant increase of the needs for accurate, reliable, and traceable measurements in any kind of industrial field, including pH measurement [1]. pH is defined as the negative logarithm of hydrogen ions activity [2]. pH measurement is carried out on a large scale ranging from laboratory level up to industry level, becoming pH is one of the most common quantitative measurements in many areas, such as agriculture, health care, biochemistry, wastewater treatment, industrial processes, research, and development and environmental monitoring [2–4]. For example, the pH value of food products is actively monitored to avoid the pathogenic microorganism growth that can damage food or adversely...
affect the taste performance and quality of the products. In the electrochemistry industry application, the plate formed will be affected by the pH of the plating solution. The incorrect pH may increase the possibility of the plate surface to peeling and produce less optimal color and final product [5].

Besides producing accurate and reliable results, the comparable result of pH measurement is necessary to prevent duplicating measurements which will consume more money and time [6]. Therefore, an accurate and reliable result of pH measurement is important as one of the parameters for quality control which will, directly and indirectly, affect every aspect of daily life and give impacts on decision-making [7]. To achieve this goal, SNSU-BSN as National Metrology Institute (NMI) for Indonesia sees the importance of the development of pH measurement infrastructure through the Electrochemistry Laboratory that is capable of providing accurate and traceable to the International System (SI) unit measurement.

NMI is a government institute appointed by national decision to hold and develop national measurement standards [8]. It holds the responsibility for establishment and maintenance of national measurement standards (primary or secondary) and methods, participation in international comparison, keep the traceability chain through dissemination of the SI unit to industry and society, ensuring the suitability of the standard for national needs, providing metrological expertise and knowledge to national users, assuring the equivalence of measurement standard, research and development in the field of metrology for government, industry, and society [1, 8-10]. The establishment of NMI in one country is very important, especially to assure the measurements used in manufacturing and international trade are accurate and traceable to the international standards [11].

Indonesia has started to establish the NMI in 2004, namely the Research Center for Calibration, Instrumentation, and Metrology (Puslit KIM–LIPI) [12], changed to Research Center for Metrology (RCM–LIPI) in 2017. However, RCM–LIPI has only capabilities in physical metrology. Therefore, the Center for Technology of Radiation Safety and Metrology/National Nuclear Energy Agency (PTKMR–BATAN) has been chosen as Designated Institute (DI) for radiation metrology and Chemical Metrology Laboratory of Research Center of Chemistry–Indonesian Institute of Science (RCCChem–LIPI) as DI for chemical metrology. Then, based on Presidential Decree No. 4/2018, the government of Indonesia has moved the task of NMI from LIPI to BSN [12, 13]. So that, RCM–LIPI and Chemical Metrology Laboratory of RCCChem–LIPI joint to BSN.

In BSN, NMI function is held by the Deputy for National Measurement Standards (SNSU-BSN), handling three fields of metrology; physical, biological, and chemical metrology. These three fields of metrology have a responsibility in research and development of their respective field, maintaining the national standard, and, especially for metrology in chemistry, providing certified reference materials (CRMs) for organic, inorganic, electrochemistry, and gas substances. Those CRMs are disseminated to the end-user or testing laboratory in Indonesia to keep the traceability chain to the SI unit. This article describe the establishment of traceability chain for pH measurement in Indonesia by the Electrochemistry Laboratory through development of the secondary method for pH measurement using differential potentiometric cell, production of various certified reference material (CRM) for buffer solution, dissemination by proficiency testing (PT) schemes for pH measurement, participation in the key comparison (KC) of APMP.QM-K91 for phthalate buffer, and the claim submission for the Calibration Measurement Capabilities (CMCs) of phthalate buffer.

2. Development of the secondary method for pH measurement
The traceability in metrology is led up to primary standard, whose quantity value is characterized by a primary measurement method, like as in pH measurement [4]. The primary measurement method for pH is based on the potential difference of the electrochemical cell without a liquid junction involving a selected buffer solution, a platinum hydrogen gas electrode, and a silver/silver chloride reference electrode, well-known as Harned Cell. This method is able to assign pH value for the primary buffer standard solution with an uncertainty value at 0.003. This primary buffer standard solutions are advantaged for the calibration of the cell without a liquid junction, as a secondary pH measurement. The cell works to assign the pH value of the secondary buffer standard solution with uncertainty
between 0.004 and 0.01. The secondary buffer standard solutions are used for calibrating commercial pH meters in common laboratories before the pH measurement in the sample [14]. This traceability guarantee that the pH measurement is reliable and valid. The metrological traceability scheme for pH is described in Figure 1.

**Figure 1.** Metrological traceability scheme for pH (Uc is expanded uncertainty with coverage factor k=2) [4].

The primary measurement method for pH is realized by NMI as the top of the traceability chain [4]. The system requires the highest degree of accuracy and the available primary buffer standard is limited and expensive. Therefore, Indonesia under RCChem-LIPI’s Electrochemistry Laboratory selected the secondary method as the highest traceability chain for pH measurement in Indonesia in 2015. In accordance with the traceability chain in Figure 1, the system is used to measure the secondary standard buffer solution with the same nominal composition as primary standard buffer solution. It used a primary buffer standard solution from primary pH measurement (Harned cell) as standard. Therefore, the secondary pH measurement is traceable to the primary buffer standard solution. The secondary standard buffer is expected to extend traceability to a greater market, offers significant economic advantages, the simpler procedure, faster, and employs cheaper instrumentation [3,14]. Then, the secondary buffer standard solutions that are produced by the Electrochemistry Laboratory can be used for calibrating the pH meter to measure the pH value of the sample and give accurate, reliable, confidence, and traceable results of pH measurement in Indonesia.

The secondary system of pH measurement developed by the Electrochemistry Laboratory was obtained from Japan. The instrument set is described in Figure 2. It consists of a U-shape cell which separated by a sintered glass disk in the middle of the cells, recognized as a Baucke cell [3]. The Baucke cell is immersed in the temperature control water bath. Each cell contains identical Platinum/Hydrogen (Pt/H2) electrodes. One cell contains a primary buffer standard solution. Then the other cell contains secondary buffer standard solutions produced by the Electrochemistry Laboratory as a sample. As a result, the secondary pH measurement is traceable to the primary buffer standard solution. These two buffers must have the same nominal composition. Moreover, gas H2 is firstly pre-humidified before entering the Baucke cell by passing through the gas into two chambers which contain similar nominal composition buffer solution to that of the sample and standard. The
Platinum/Hydrogen (Pt/H$_2$) electrodes then connected into the multimeter and the potential difference between two Pt/H$_2$ electrodes is measured. The detailed procedure of pH measurement using the secondary pH measurement system is described in the previous report [15]. The pH of the secondary buffer standard solutions is calculated using Equation (1) [3]. $\text{pH}_s$ stands for pH value from the primary buffer standard solution, $\Delta E_{cell}$ represents the potential difference between two Pt/H$_2$ electrodes, $F$ is Faraday constant, $R$ is the universal gas constant, and $T$ defines temperature (Kelvin).

$$\text{pH}_s = \text{pH}_p - \frac{\Delta E_{cell} F}{RT \ln 10}$$

![Diagram of the secondary pH measurement system](image)

**Figure 2.** The secondary pH measurement system: (A) hydrogen gas, (B) gas controller, (C1&C2) chambers contain buffer, (D) Baucke cell with Pt electrodes, (E) multimeter, (F) thermometer, (G) water bath [15].

Before routine usage, this secondary pH measurement must be validated to confirm that the method is suitable for intended use as required in ISO/IEC 17025:2017. The results of the validation method for secondary pH measurement described in the previous experiment [15]. The results showed that the accuracy and precision of the method were sufficiently satisfying, with an estimated uncertainty value of 0.001 (k=2) which is a contribution of the primary buffer standard solution (56%), potential (43%), and temperature (1%) for secondary pH measurement at 25°C. Afterward, this method can be routinely used to measure the pH value of secondary buffer standard solutions.

### 3. Production of CRM for Buffer Solution

CRM is a reference material that has been characterized and accompanied by a certificate that provides the value of the specified property, its uncertainty, and the statement of traceability [16]. It plays a vital role in the quality of measurement, such as in pH measurement. It is used for calibration of instruments, assessment of the measurement method, and establishment of the measurement traceability results [17]. The production and certification of RM is a key activity of NMI to improve and maintenance of a worldwide coherent system of measurement [18].
The Electrochemistry Laboratory has started to do the research and development in produce CRM for buffer solution since 2013. The characterization, homogeneity, and stability of CRM buffer were conducted based on ISO Guide 35. In the beginning, a pH meter was used by the Electrochemistry Laboratory to measure the pH value of the CRM buffer. Various buffers have been produced, including oxalate (1.68 ± 0.03), phthalate (pH 4.00 ± 0.02), phosphate (pH 6.86 ± 0.02), and borate buffer (pH 9.18 ±0.03) at 25°C [19, 20]. This CRM buffer, however, has big uncertainty. In order to reduce the uncertainty, the Electrochemistry Laboratory started to produce CRM for buffer solution using secondary pH measurement system with a lower uncertainty in 2015. The buffers produced with this method consist of phthalate (pH 4.005 ± 0.004) and phosphate (pH 6.863± 0.004). The availability of CRM buffer in Indonesia is expected to fulfill the local needs, suppress import value, and provide the traceability of pH measurement in Indonesia to get accurate, reliable, confidence, and traceable results. The CRM buffer that has been produced by the Electrochemistry Laboratory is shown in Figure 3.

Figure 3. CRM buffer of the Electrochemistry Laboratory and its packaging.

4. Proficiency Testing Providing
Proficiency Testing (PT) is an evaluation of laboratory performance against pre-establish criteria by means of interlaboratory comparisons [21]. It is aimed to monitor laboratories work and compare their results with other laboratories and is a part of the process in assessing the capability of laboratories to perform measurements and tests for which accreditation is intended [22].

PT scheme for pH commodity in Indonesia has been conducted by the chemical metrology laboratories since the laboratory was under RCChem–LIPI. At the first, chemical metrology laboratories only provide the PT samples individually. Beginning in 2008, the PT scheme has been integrated with National Accreditation Committee (KAN) program, marking the RCChem’s chemical metrology laboratory is one of the PT providers in Indonesia, which is responsible to process participant data and evaluate the their performance. This activity becomes an annual agenda, serving different commodities and parameters each year, to disseminate the traceability to laboratories in Indonesia through PT sample or standard solution (packaged together with PT sample). The PT scheme for pH measurement that has been conducted by the Electrochemistry Laboratory is tabulated in Table 1.

Table 1. PT scheme for pH measurement that has been conducted by the Electrochemistry Laboratory.

| Year | Commodities                                      | Participants |
|------|--------------------------------------------------|--------------|
| 2013 | Phthalate (pH 4.04) and phosphate buffer (pH 6.56) | 10           |
| 2014 | pH in wastewater (pH 1.91)                       | 94           |
| 2015 | Citrate buffer (pH 4.92)                         | 36           |
| 2016 | Borate buffer (pH 9.186)                         | 50           |

The increasing number of laboratories participating in this proficiency test shows that the laboratory realizes the importance to participate in proficiency testing. It is one of kind to assure the quality of test and calibration results as mention in ISO 17025 [23]. The PT results could be a self-evaluation for each laboratory. The satisfactory results show the performance of the laboratory is
good, while for unsatisfactory results means failure to attain the minimum satisfactory score for an analyte, test, subspecialty, or specialty for a testing event. This may also be referred to as unacceptable performance and the laboratory must take the evaluation for improving their performance [24].

5. Participating in the Key Comparison (KC) and Claiming the Calibration and Measurement Capability (CMC)

KCs are international inter-laboratory studies used to establish the degree of equivalence between national measurement standards that carried out by an NMI. Participation in KCs for NMI is the best way to demonstrate the NMI confidence in its measurement results and consequently, in its measurement capabilities [25]. Therefore, the measurement results obtained will be internationally comparable and accepted, giving no need to duplicate the measurement in other countries.

The basis for working international trades, commerce, and regulatory affairs is the presence of mutual recognition in calibrations, measurements, and test certificates [26,27]. KC plays an important role to enable that mutual recognition framework. As an international inter-laboratory study, KCs establish the degree of equivalence between national measurement standards that carried out by an NMI. From the analysis of the key comparison result, the corresponding measurement capability of NMIs is validated and it will be written as calibration and measurement capabilities (CMCs) [27].

Comparability and traceability are normally established through participation in KC organized by regional or international metrology organizations like the International Bureau of Weights and Measures (BIPM) and the Asia Pacific Metrology Programme (APMP) [28]. The Electrochemistry Laboratory as part of NMI focuses on the study of comparability and traceability of pH measurements participated in the KC of APMP.QM-K91 in 2015. This was organized by TCQM of APMP to test the abilities of NMI in the APMP region to measure the pH value of phthalate buffer. This comparison was coordinated by NMIJ (National Metrology Institute of Japan). The sample was phthalate buffer with molality 0.05 mol/g prepared in a polyethylene bottle. There were 12 NMIs that participated in this KC, including the Electrochemistry Laboratory that still under the RCChem–LIPI at that time. In the KC, the Electrochemistry Laboratory employed the above-mentioned secondary pH measurement system to measure the sample of phthalate buffer. The measured value of phthalate buffer at 25°C (4.006) is close to the Key Comparison Reference Value (KCRV) (4.00765) as described in Figure 4 [29,30], showing the satisfactory of the measurement. This good results from APMP.QM-K91 can be used by the Electrochemistry Laboratory to support the CMC claim for a phthalate buffer using secondary pH measurement method (Differential Potentiometric Cell), beside the proof of the dissemination activity in national PT.

Figure 4. Results of pH measurement for phthalate buffer at 25°C compared with KCRV of APMP.QM-K91 [29, 30].
After the peer-review evaluation and document process as required, the Electrochemistry Laboratory has successfully been granted the CMC by BIPM in 2018 for pH of phthalate buffer (pH 3.97-4.03) with expanded uncertainty 0.004 [31]. The list of CMCs of all countries is openly available to customers as published in the BIPM key comparison (KCDB) of the CIPM MRA [32]. It is mainly aimed to inform customers about quantities, ranges, and achievable uncertainty of the measurement laboratory [33].

6. Conclusion
The establishment of traceability chain for pH measurement in Indonesia by Electrochemistry Laboratory is at the beginning level to accommodate the laboratory needs. The Electrochemistry Laboratory has conducted various research activities from 2015 to build the traceability chain of pH measurement in Indonesia. The activities cover the development of the secondary method for pH measurement, the production of CRM for buffer solution, the organization of the PT scheme, the participation in the KC, and finally the claim of the CMC. All activities in the efforts to develop metrology in chemistry in Indonesia, to build the pH measurement infrastructure, and furthermore, to support the quality assurance and the global trade. The metrological research will be continued in the short-term and long-term plan to another pH level and other electrochemical measurands.

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