

VALIDATION OF A SECONDARY METHOD USING JONES CELL - TYPE D FOR ELECTROLYTIC CONDUCTIVITY MEASUREMENTS

VALIDASI METODE SEKUNDER MENGGUNAKAN SEL JONES TIPE D UNTUK PENGUKURAN KONDUKTIVITAS ELEKTROLITIK

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ABSTRAK

Parameter konduktivitas elektrolitik sangat berguna dalam menentukan kualitas air yang digunakan di berbagai industri. Pengukuran konduktivitas elektrolitik dilakukan dengan menggunakan alat konduktometer yang telah dikalibrasi dengan bahan acuan bersertifikat. Saat ini bahan acuan bersertifikat (CRM) masih merupakan barang impor. Oleh karena itu, Laboratorium Elektrokimia SNSU-BSN telah mengembangkan metode sekunder untuk mengukur konduktivitas elektrolitik dalam bahan acuan untuk dijadikan sebagai CRM. Metode sekunder yang digunakan adalah metode dengan menggunakan sel Jones tipe D untuk rentang pengukuran 20 – 150 mS/cm. Validasi metode sekunder dibahas dalam makalah ini. Parameter pengujian meliputi linearitas, akurasi, presisi-*repeatability*, dan estimasi ketidakpastian pengukuran. Hasil validasi diperoleh linearitas yang baik dengan nilai R^2 sebesar 0,999 pada frekuensi 120 – 480 Hz. Akurasi dan presisi cukup memuaskan dengan nilai bias 0,01 mS/cm dan RSD 0,031%. Nilai ketidakpastian diperluas dari metode ini dievaluasi sebesar 0,15% ($k=2$). Pengukuran konduktivitas elektrolitik ini tertelusur ke satuan SI melalui bahan acuan primer CRM1714 dari Lembaga Metrologi Nasional Denmark. Metode ini telah digunakan untuk mensertifikasi bahan acuan sekunder KCl 1 M, dengan nilai 111,6 mS/cm dan ketidakpastian diperluas relatif 0,15%. Bahan acuan sekunder ini telah dibuat oleh Laboratorium Elektrokimia SNSU-BSN yang bertujuan untuk mendiseminasikan ketertelusuran pengukuran konduktivitas elektrolitik di Indonesia dan mengurangi ketergantungan pada bahan acuan impor yang membutuhkan waktu lebih lama dan biaya tinggi.

Kata Kunci: Pengukuran konduktivitas elektrolitik, Metode sekunder, Akurasi, Presisi, Ketidakpastian pengukuran

ABSTRACT

The electrolyte conductivity parameter is very useful in determining the quality of water used in various industries. Electrolyte conductivity measurements are carried out using a conductivity meter device that has been calibrated with certified reference materials. Currently, certified reference materials (CRM) are still imported goods. Therefore, the SNSU-BSN Electrochemical Laboratory has developed a secondary method for measuring conductivity in reference materials to provide the CRM. The secondary method used is a method using Jones-type cell D for a measurement range of 20–150 mS/cm. The validation of the secondary method in describing its performance is discussed in this paper. The test parameters include linearity, accuracy, precision-repeatability, and estimation of measurement uncertainty. The validation results obtained good linearity with an R^2 value is 0.999 at a frequency 120-480 Hz. Accuracy and precision are quite satisfactory, with a bias value of 0.01 mS/cm and an RSD of 0.031%. The expanded uncertainty value of this method was evaluated at 0.15% ($k=2$). This electrolytic conductivity measurement was traceable to SI units via the primary reference material CRM1714 from the Danish National Metrology Institute. This method has been applied to certify the secondary reference material KCl 1 M, with a value of 111.6 mS/cm and a relative expanded uncertainty of 0.15%. This secondary reference material has been prepared by the Electrochemistry Laboratory of SNSU–BSN, which is intended to disseminate traceability of electrolyte conductivity measurements in Indonesia and reduce dependency on imported reference materials that require longer time and high costs.

Keywords: *Electrolytic conductivity measurement, Secondary method, Accuracy, Precision, Measurement uncertainty*

1. INTRODUCTION

The electrolytic conductivity represents the charge conductible capacity of ions in electrolytic solution. The magnitude of the electrolytic conductivity can indicate the number of ions or substances that are ionized in the solution. The more ions in the solution, the higher the electrolytic conductivity; the fewer ions in the solution, the lower the electrolytic conductivity (Su et al., 2019; Fondriest Environmental, 2014). Electrolytic conductivity is a non-specific parameter that can be used to estimate the concentration of ionized substances in solution. The electrolytic conductivity parameter has been widely used and applied in various industries as a measure of water quality. In the pharmaceutical, semiconductor, and power generation industries, electrolytic conductivity is used to assess the purity of the water used (Uysal, E et al., 2020). In the environmental field, conductivity is used as one of the parameters in environmental water quality monitoring. This parameter is also used to evaluate water quality based on regulations and standards, such as drinking water and water used in the food and health care industries (Orrù, 2014). Based on WHO, the importance of electrolytic conductivity in determining water

quality such as in drinking water, valid and accurate results of electrolytic conductivity measurements are needed (Meride, Y and Ayenew, B, 2016).

Accurate measurement results can be obtained using the proper method and have been proven through a series of validation processes as required in SNI ISO/IEC 17025:2017. Validation is confirmation through examination and provision of objective evidence that the specific requirements for its intended use have been met (Eurachem, 2014; Faridah et al., 2018). In addition, the validity of the test results, as stated in SNI ISO/IEC 17025:2017 clause 6.5, that is, the laboratory must ensure that the test results are traceable to International Units (SI), either through calibration provided by a competent laboratory or certificate value from reference materials provided by competent manufacture and traceable to SI (Faridah et al., 2018).

The calibration for electrolytic conductivity measurements is basically a measurement of the cell constant, and the measurement can be carried out by several methods, such as the primary method (which is directly traceable to the SI and typically produces the primary reference material), a secondary method (which is traceable to primary reference material), and tertiary method

using a commercial conductometer (which is traceable to secondary reference material and produces technical reference material used to measure samples) (ZMK, 2021). Since establishing a primary method for electrolytic conductivity measurements is not easy and requires high-cost procedures, the development of competency in the secondary measurement is an excellent step to start the dissemination of electrolytic conductivity measurements at the national level.

The Electrochemistry Laboratory of SNSU–BSN (formerly the Laboratory under Indonesian Institute of Sciences) started developing the infrastructure for electrolytic conductivity measurement in 2017. One of the previous works covered the accuracy and precision study of electrolytic conductivity measurement by using Jones cell-type E (Hindayani, A & Hamim, N, 2022).

Herein, the validation of a secondary method for determining electrolytic conductivity using Jones cell-type D is presented. A Jones cell-type D is a glass tubular cell with two platinization electrodes having a diameter of 20 mm and a distance between the two electrodes of 60 mm. While Jones cell-type E can be operated to measure electrolytic conductivity at 100 $\mu\text{S}/\text{cm}$ -

1 mS/cm , Jones cell-type D has operating ranges at 20 mS/cm -150 mS/cm (Breuel et al., 2008). This secondary method is the first established in Indonesia regarding the authors' knowledge. The validation process evaluated linearity, accuracy, precision (repeatability), and measurement uncertainty estimation. The validated method is a fundamental competency for Electrochemistry Laboratory of SNSU–BSN for further works in certified reference material (CRM) preparation, especially electrolytic conductivity at a secondary level. Providing CRM for electrolytic conductivity in Indonesia is very important, considering testing laboratories in Indonesia widely used the CRM to calibrate the conductometer and reducing the dependency on imported supplies that require higher costs and take a long time.

2. LITERATUR REVIEW

The magnitude of the electrolytic conductivity is influenced by the nature of the ion (charge, size, and mobility) and the nature of the solvent (viscosity and dielectric constant) (Orrù, 2014). The measurement of electrolytic conductivity with the primary method defines K_{Cell} , which through the physical dimensions of the cell geometry, by

measuring the distance between the two electrodes (l) and the electrode area (A), according to equation (3). The value of R observed in this situation is traceable directly to the SI, so the electrolytic conductivity of the sample can be determined in absolute terms. Thus, this method is categorized as a primary method (Brinkmann et al., 2003).

The amount of electrolytic conductivity is determined by measuring a solution's resistance (R) using a conductivity cell. The magnitude of R is directly proportional to the effective distance between the two electrodes (l) and inversely proportional to the electrode area (A) according to equation [1], where ρ is resistivity (Ωm), which is a constant whose magnitude is specific for a particular type of solution

$$R = \rho \times \frac{l}{A} \quad [1]$$

The value of κ is inversely proportional to the ρ , as seen in equation [2].

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} \quad [2]$$

Each cell used to measure electrolytic conductivity has a cell constant value (K_{Cell}) which is calculated using equations [3] or [4], where G (conductance) with Siemens units (S) is the inverse of resistance (R) with units of Ohms (Ω), following equation [5].

$$K_{\text{Cell}} = \frac{l}{A} \quad [3]$$

$$K_{\text{Cell}} = \frac{\kappa}{G} \quad [4]$$

$$G = \frac{1}{R} \quad [5]$$

So, the electrolytic conductivity of the solution can be calculated using the equation [6]

$$\kappa = K_{\text{Cell}} \times G \quad [6]$$

(Krismastuti, F.S.H et al.,2019, Shreiner & Pratt, 2004)

The measurement of electrolytic conductivity with the primary method defines K_{Cell} , which through the physical dimensions of the cell geometry, by measuring the distance between the two electrodes (l) and the electrode area (A), according to equation [3]. The value of R observed in this situation is traceable directly to the SI, so the electrolytic conductivity of the sample can be determined in absolute terms. Thus, this method is categorized as a primary method (Brinkmann et al., 2003).

In the secondary method developed in this work, K_{Cell} is calibrated with the primary reference material by measuring the R value of the reference material so that the K_{Cell} value is obtained based on equation (4). This method is traceable to the primary reference material, so it is categorized as a secondary method (Breuel et al., 2008).

Temperature is very important and affect the measurement of electrolytic conductivity. An increase in temperature

in the solution will cause a decrease in viscosity, an increase in the mobility of ions in solution and an increase in the number of ions in solution due to molecular dissociation which in turn will increase the value of the electrolytic conductivity of the solution (Barron and Ashton, 2013). For example, the electrolytic conductivity value for a 0.01 M KCl solution at 20°C has a value of 1.273 mS/cm, while at 25°C it has a value of 1.408 mS/cm (Wu et al., 1991). Furthermore, the concept of reference temperature is known to compare the results of electrolytic conductivity obtained at different temperatures. The reference temperature is usually 20°C or 25°C. The effect of temperature on the measurement of electrolytic conductivity is expressed in equation [7] (Tangpaisarnkul, 2017).

$$\kappa = K_{sel} \times G (1 + TK \times \Delta T) \quad [7]$$

Where :

TK is the temperature coefficient

ΔT is the difference between the measured temperature and the reference temperature.

The conductivity meter measures the electrolytic conductivity at the measured temperature and will correct its value to the reference temperature using the temperature correction function (Radiometer, 2004).

3. EXPERIMENTAL SECTION

Materials and Instruments

As a primary reference material, CRM1714 was purchased from DFM Denmark (certified value as 100 mS/cm at 25°C). CRM1714 was used to determine linearity and K_{Cell} . A secondary reference material D-RM-15186-01-00 was obtained from ZMK & Analytik GmbH Germany (certified value as 111.60 mS/cm at 25°C with an expanded uncertainty of 0.20%). The secondary reference material was employed for the determination of accuracy and precision.

The measurement of the electrolytic conductivity was performed by a secondary method using a Jones cell, according to Breuel's work (Breuel et al., 2008). A Jones cell-type D was used to cover electrolytic conductivity measurements at 20–150 mS/cm. The primary reference material CRM1714 and the secondary reference material D-RM-15186-01-00 were measured for resistance (R) using an LCR meter (8105G, GW-Instek Taiwan) equipped with a water bath and chiller (Proline PV36 and DLK25, Lauda Germany), digital thermometer (MKT50, Anton Paar Germany equipped with Pt 1000 sensor) and Jones cell-type D was purchased from ZMK & Analytik GmbH, Germany. A set of secondary

measurement systems for electrolytic conductivity is shown in Figure 1 (Hindayani, A & Hamim, N, 2022).

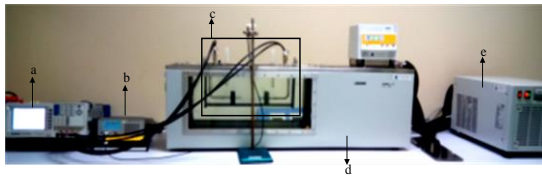


Figure 1. A set system of electrolytic conductivity secondary measurement system: a) LCR meter, b) thermometer, c) Jones cell-type D, d) waterbath, e) chiller

Electrolytic Conductivity Measurement

The solution to be measured was placed in a Jones cell-type D and kept at 25°C with a water bath. The resistance of the solution was measured using an LCR meter at the most linear measurement frequency, and a $1/f$ (Hz^{-1}) curve was plotted against R (Ω). After obtaining a linear line equation, the intercept value was used as the average resistance value of the measurement and converted to conductance (G) using equation [5]. Then, the value of the electrolytic conductivity of the solution was calculated using equation [6] with previously obtained K_{Cell} .

Every cell in the conductivity measurement, including the Jones cell-type D, has a K_{Cell} value used to calculate the value of the electrolytic conductivity as in the equation. K_{Cell} in a Jones cell-type D or a secondary method

cell is determined by analyzing CRM, which has a certified electrolytic conductivity value. In this study, CRM1714, with an electrolytic conductivity value of 100 mS/cm at 25°C (Snedden, 2017), was advantaged to determine the K_{Cell} of the used cell with the same procedure.

Method Validation

The secondary method using a Jones cell-type D was validated first to ensure that the measurement results obtained were accurate and reliable before measuring the electrolytic conductivity reference material produced (Gupta, P.C, 2015). Parameters studied in the validation included linearity, accuracy, repeatability, and measurement uncertainty.

Determination of frequency range

Determination of working frequency range in validating the electrolytic conductivity measurement method using Jones cell-type D was carried out to obtain the most linear frequency because selecting the appropriate frequency range is critical to obtaining accurate electrolytic conductivity measurement results (Breuel et al., 2008). Measurements were made by measuring the resistance (R) of the CRM1714 primary reference material using an LCR

meter at a frequency (f) of 20-2000 Hz. A regression curve is made between $1/f$ (Hz^{-1}) against R (Ω), following the evaluation of a line equation and its linear regression coefficient (R^2). The criteria for the curve are said to be linear if it has a value of $R^2 = 0.99$ (UNODC, 2009). Furthermore, the most linear measurement frequency was used to determine the K_{Cell} and for further studies in the validation.

Accuracy

Accuracy is the closeness of agreement between a measured quantity value and a true quantity value of a measurand (Eurachem, 2011). In this case, the secondary reference material D-RM-15186-01-00 from ZMK & Analytik GmbH was used to determine the method's accuracy. The determination of accuracy is evaluated by comparing the average measurement results of the reference material (\bar{X}) with the value of the certificate ($X_{\text{reference material}}$) (Gupta, P.C, 2015). The difference between the values was named bias (b) and calculated quantitatively based on equation [8]. A method is indicated to be accurate if it meets the criteria $-2\sigma < b < 2\sigma$ (Budiman, 2014). The value of σ is calculated using equation [9], where $u_{\text{ref material}}$ denotes the standard uncertainty of the reference material from the

certificate, s_w denotes the standard deviation of the measurement of the reference material, and n denotes the number of measurements.

$$b = |\bar{X} - X_{\text{reference material}}| \quad [8]$$

$$\sigma = \sqrt{u_{\text{Ref material}}^2 + \frac{s_w^2}{n}} \quad [9]$$

Precision

Precision is the closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions (Eurachem, 2011).

In this study the precision was expressed with repeatability test and was carried out by measuring the secondary reference material D-RM-15186-01-00 as much as 12 times by the same analyst, method, tool, and time. The %RSD (relative standard deviation) was calculated using equation [10].

$$\%RSD = \frac{\text{Standard deviation}}{\bar{x}} \times 100 \quad [10]$$

Measurement Uncertainty

The estimation of measurement uncertainty is based on the guidelines using a bottom-up approach. The steps in uncertainty estimation include determining the measurement method, identifying sources of uncertainty, characterizing sources of uncertainty, calculating standard uncertainty (u),

calculating combined uncertainty (u_c), and calculating expanded uncertainty (U) (EURACHEM/CITAC Working Group, 2012).

4. RESULTS AND DISCUSSION

The measurement of electrolytic conductivity using a secondary method is the measurement system with the highest traceability so far in Indonesia that is traceable to SI. The traceability pyramid for measuring electrolytic conductivity in Indonesia is shown in Figure 2. The secondary reference material produced by Electrochemistry Laboratory of SNSU-BSN is expected to be used to calibrate the conductometer used by testing laboratories in Indonesia, as the responsibility of the National Metrology Institute (NMI) in developing and maintaining national measurement standards as well as providing internationally recognized traceability to SI (EURAMET e.V., 2015). So it can be said that the results of electrolytic conductivity measurements in the testing laboratory are traceable with unbroken chain to SI unit through primary CRM of DFM via Electrochemistry Laboratory of SNSU-BSN.

Before the application of secondary measurement system to determine the electrolytic conductivity

of the secondary reference material produced by Electrochemistry Laboratory of SNSU-BSN, validation of the method was first carried out, which included linearity, accuracy, precision (repeatability), and the estimation of measurement uncertainty.

Before the application of secondary measurement system to determine the electrolytic conductivity of the secondary reference material produced by Electrochemistry Laboratory of SNSU-BSN, validation of the method was first carried out, which included linearity, accuracy, precision (repeatability), and the estimation of measurement uncertainty.

In determining linearity, three measurements were made with different frequency ranges, where the first, the second, and the third measurement used a frequency of 120–2000 Hz^{-1} , 20–660 Hz^{-1} , and 120–480 Hz^{-1} , respectively, as can be shown on Figure 3-5. From the three measurements with different frequency ranges, the R^2 value in the third measurement with frequency 120–480 Hz^{-1} was close to 1. Furthermore, the frequency of 120–480 Hz^{-1} was used to determine K_{Cell} and the conductivity of the secondary reference material in accuracy and precision studies.

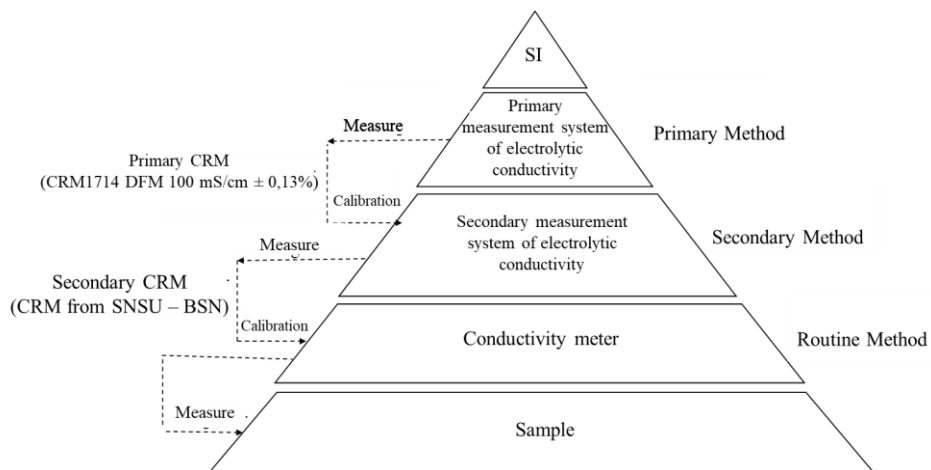


Figure 2. Pyramid of traceability of electrolytic conductivity measurement in Indonesia

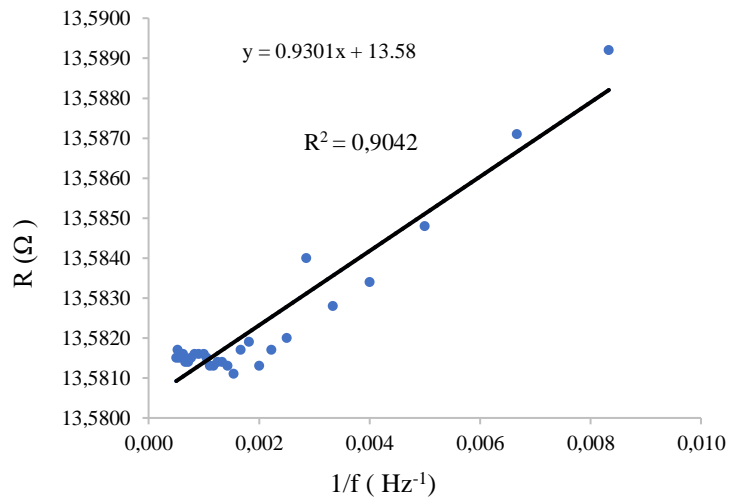


Figure 3. Linearity at the frequency of 120–2000 Hz

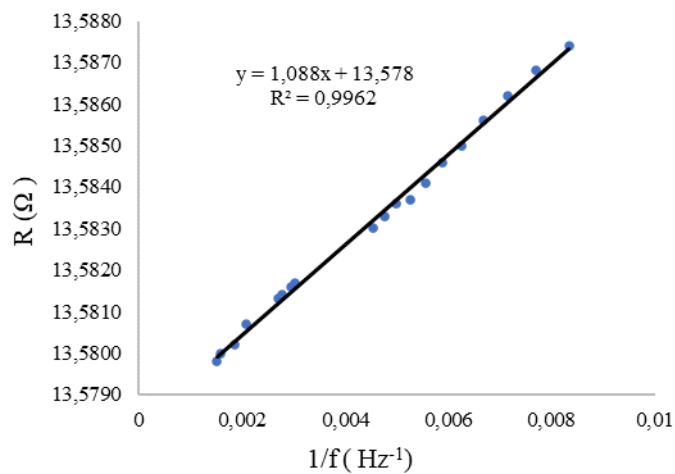


Figure 4. Linearity at the frequency of 20–660 Hz

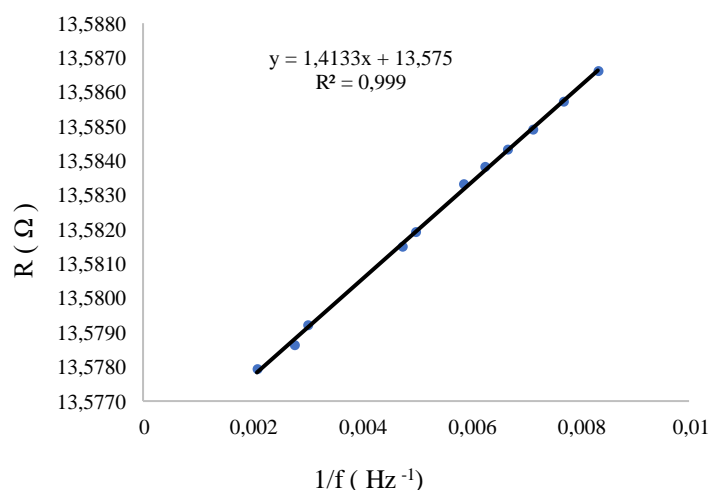


Figure 5. Linearity at the frequency of 120–480 Hz

The measurement results of the Jones cell-type D's K_{Cell} using optimized frequency are described in Table 1. The average value from measurements (1.5167 cm^{-1}) was taken as the specific cell constant of the Jones cell-type D used in this study, and the value was used to calculate the electrolytic conductivity value of the secondary reference material (D-RM-15186-01-00), as summarized in Table 2.

Table 1. The results of determining K_{Cell} of Jones cell-type D

No. Measurement	R (Ω)	G (mS)	K_{Cell} (cm^{-1})
1	15.519	65.967	1.5159
2	15.166	65.937	1.5166
3	15.167	65.933	1.5167
4	15.176	65.894	1.5176
5	15.166	65.937	1.5166
Average			1.5167

The test for accuracy and precision was performed by measuring the resistance and calculating the κ value of the secondary reference material using the above equations at 12-time experiments. The accuracy was evaluated by determining measurement bias from the comparison between the measurement result of the reference material and the certificate value. This value meets the criteria of $-2\sigma < b < 2\sigma$. Therefore, it can be assumed that the secondary method of measuring electrolytic conductivity using Jones cell-type D is accurate. The repeatability test gave good results with a low %RSD value, i.e., 0,031%.

Uncertainty is a non-negative parameter that describes the distribution of the quantitative value of a measurement result (EURACHEM/CITAC Working Group, 2012). Uncertainty is essential to

the measurement because many factors influence and contribute to measurement results. Contributing factors can come from the tools and materials being measured, the environmental conditions of the measurement, the analyst who performs the measurement, and other sources. Sources of uncertainty associated with measurement can be divided into two types, type A and type B sources of uncertainty. Type A sources of uncertainty caused by random effects generally come from the standard deviation of a series of measurements performed under the same conditions (repeatability). This effect causes an error that varies from measurement to measurement. Meanwhile, the type B measurement uncertainty, also known as the systematic effect, produces a constant error in the repetition time scale. The measurement uncertainty caused by this systematic effect can come from the instrument's resolution or the data on the calibration certificate. (EURACHEM/CITAC Working Group, 2012).

Table 2. Measurement results secondary reference material D-RM-15186-01-00

No. Measurement	R (Ω)	G (mS)	κ D-RM-15186-01-00 (mS/cm)
1	13.598	73.540	111.54
2	13.593	73.567	111.58
3	13.585	73.611	111.65
4	13.586	73.605	111.64
5	13.587	73.600	111.63
6	13.587	73.600	111.63
7	13.586	73.605	111.64
8	13.594	73.562	111.57
9	13.587	73.600	111.63
10	13.587	73.600	111.63
11	13.586	73.605	111.64
12	13.593	73.567	111.58
Average of measurement result (\bar{x})			111.61
$X_{\text{reference material}}$			111.60
b^*			0.01
$U_{\text{CRM}} - \text{D-RM-15186-01-00}$			0.1
N			12
σ^{**}			0.1
criteria $-2\sigma < b < 2\sigma$			OK
Deviation standard (S_w)			0.035
% RSD^{***}			0.031

* calculated using equation [8]

** calculated using equation [9]

*** calculated using equation [10]

There are two steps in estimating the uncertainty of the secondary method of measuring electrolytic conductivity in this study, including measuring K_{Cell} and determining the electrolytic conductivity. The components contributing to the uncertainty K_{Cell} measurement are derived from equation [7] (Tangpaisarnkul, 2017). Based on the equation, the measurement uncertainty of K_{Cell} cover uncertainties from (a) primary reference material's conductivity (κ ref-type B); (b) conductance (derived from the uncertainty of the LCR meter calibration certificate (G-type B), the uncertainty of extrapolation to the conductance value measurement curve (extrapolation-type A), and uncertainty of the conductance measurement repeatability (G-type A)); (c) the difference in temperature (derived from the uncertainty of thermometer (Thermometer-type B), the repeatability of the temperature measurement (Temperature-type A), the temperature homogeneity on the water bath (T hom-type B), and the stability of the water bath (T stab-type B)); and (d) the temperature coefficient (TK-type B) from the certificate (Snedden, 2017).

For the uncertainty of κ value measurement, the components that

contribute to the κ value are based on equation [11] (Tangpaisarnkul, 2017), where δCO_2_{eq} is CO_2 equilibrium, $\delta CO_2_{sens\ coef}$ is CO_2 sensitivity coefficient, and $\delta CO_2_{sup\ factor}$ is CO_2 suppression factor. As written from the equation, the measurement uncertainty of κ arises from (a) the calculated K_{Cell} uncertainty (K_{Cell} - type B); (b) conductance (derived from the uncertainty of the LCR meter calibration certificate (G-type B), the uncertainty of extrapolation to the conductance value measurement curve (extrapolation-type A), and uncertainty of the conductance measurement repeatability (G-type A)); (c) the difference in temperature (derived from the uncertainty of thermometer (Thermometer-type B), the repeatability of the temperature measurement (Temperature-type A), the temperature homogeneity on the water bath (T hom-type B), and the stability of the water bath (T stab-type B)); (d) the temperature coefficient (TK-type B) from the certificate (Snedden, 2017); (e) CO_2 equilibrium value; (f) CO_2 sensitivity coefficient; and (g) CO_2 suppression factor obtained from the literature (CO_2 -type B).

$$\kappa = K_{Cell} \times G(1 + TK \times \Delta T) + \frac{\delta CO_2_{eq} \times \delta CO_2_{sens\ coef}}{\delta CO_2_{sup\ factor}} \quad [11]$$

The uncertainty estimation of K_{Cell} determination and the κ value measurement by the secondary method using the Jones cell has been discussed in the previous literature (Hindayani et al., 2019). However, there is a revision related to the source of uncertainty from the repeatability uncertainty and the temperature coefficient components. The uncertainty estimation of the K_{Cell} Jones cell-type D measurement and the measurement of the κ value of the secondary reference material D-RM-15186-01-00 are listed in Tables 3 and 4.

From Table 4, it is found that the value of the uncertainty of measuring the electrolytic conductivity of the secondary reference material D-RM-15186-01-00 is 0.15%, where the most significant contribution of uncertainty comes from K_{Cell} (90.20%), thermometer (4.27%), and G measurement repeatability (G-type A) (2.73%). In the uncertainty estimation results, it can be seen that the uncertainty value of the measurement results is smaller (0.15%) when compared to the uncertainty value of the certificate of reference material DFM-D-RM-15186-01-00 (0.20%). The smaller uncertainty condition in this study is

caused by the uncertainty value of the measurement results was only from the uncertainty value of the measurement characteristics, while to determine the uncertainty of reference material, there are sources of uncertainty originating from the homogeneity and stability of the reference material that must be taken into account.

The validation results of the secondary method of measuring electrolytic conductivity showed a good performance. This method has been applied to characterize the secondary reference material prepared by the Electrochemistry Laboratory of SNSU-BSN. Reference materials for electrolytic conductivity are generally made from KCl solution with different electrolytic conductivity values depending on the conductivity value of the sample to be measured (Brinkmann et al., 2003; Shreiner & Pratt, 2004). In this application, the conductivity value of the KCl 1 M reference material was assigned at 111.6 mS/cm, which was traceable to SI through the primary reference material from DFM. The relative expanded measurement uncertainties for the CRM were found to be 0.15 % at a confidence level of approximately 95 % ($k=2$).

Table 3. Estimation of measurement uncertainty in K_{Cell} determination of Jones cell-type D

Sources of Uncertainty	Value (Xi)	Divisor	Uncertainty	unit	Sensitivity Coefficient (ci)	unit	standard uncertainty (ui)	unit	Contribution (ci x ui) ² (cm ⁻¹)
K_{ref} - Type B	100	2	0.13	mS/cm	0.0152	1/mS	6.50×10^{-2}	mS/cm	9.76×10^{-7}
G - Type B	65.934	2	0.01582	mS	0.023	1/mS cm	7.91×10^{-3}	mS	3.31×10^{-8}
Extrapolation - Type A	1	1	0.00018	mS	0.023	1/mS cm	1.80×10^{-4}	mS	1.71×10^{-11}
G - Type A	65.934	5	0.026	mS	0,023	1/ms cm	5.20×10^{-3}	mS	1.43×10^{-8}
Temperature-Type A	0.0037	5	0.0023	K	0.0297	1/cm K	4.60×10^{-4}	K	1.87×10^{-10}
Thermometer- type B	0.0037	2	0.0153	K	0.0297	1/cm K	7.65×10^{-3}	K	1.00×10^{-7}
T stab -Type B	1	1.732	0.003	K	0.0297	1/cm K	1.73×10^{-3}	K	2.64×10^{-9}
T hom -Type B	1	1.732	0.004	K	0.0297	1/cmK	2.31×10^{-3}	K	4.71×10^{-9}
TK-Type B	0.0196	1.732	0.00098	1/K	0.00561	K/cm	5.70×10^{-4}	1/K	1.02×10^{-11}
Sum of Square									1.08×10^{-6}
combined uncertainty (Root of sum square)									1.04×10^{-3}
Expanded Uncertainty (U, k=2)									2.08×10^{-3}

Table 4. Estimation of measurement uncertainty in electrolytic conductivity measurement

Sources of Uncertainty	Value (Xi)	Divisor	Uncertainty	Unit	sensitivity coefficient (ci)	unit	standard uncertainty (ui)	unit	contribution (ci x ui) ² (cm ⁻¹)
K _{cell} -Type B	1.5167	2	0.0021	1/cm	73.6025	mS	1.05x10 ⁻³	1/cm	5.97x10 ⁻³
G -Type B	73.5926	2	0.0158	mS	1.517	1/cm	7.90x10 ⁻³	mS	1.44x10 ⁻⁴
G - Type A	73.5926	3.4641	0.0307	mS	1.517	1/cm	8.90x10 ⁻³	mS	1.81x10 ⁻⁴
Extrapolation- Type A	1	1	0.0003	mS	1.517	1/cm	3.00x10 ⁻⁴	mS	2.07x10 ⁻⁷
Thermometer -Type B	0.0068	2	0.01530	K	2.1988	mS/cm K	7.60x10 ⁻⁴	K	2.82x10 ⁻⁴
Temperature -Type A	0.0068	12	0.0022	K	2.1988	mS/cm K	2.00x10 ⁻⁴	K	1.62x10 ⁻⁷
T stab- Type B	1	1.7321	0.0030	K	2.1988	mS/cm K	1.70x10 ⁻³	K	1.45x10 ⁻⁵
T hom - Type B	1	1.7321	0.0040	K	2.1988	mS/cm K	2.30x10 ⁻³	K	2.58x10 ⁻⁵
TK - Type B	0.0196	1.7321	0.00098	1/K	7.59E-01	mS K/cm	6.00x10 ⁻⁴	1/K	2.07x10 ⁻⁷
CO ₂ equilibrium - Type B	0	1.7321	50.0000	ppm	2.2E-05	mS/cm/ppm	28.8675	ppm	4.03x10 ⁻⁷
CO ₂ sens coeff - Type B	0.0011	1.7321	0.0010	mS/cm/ppm	0		2.88x10 ⁻⁴	mS/cm/ppm	0
CO ₂ suppression- Type B	50	1.7321	0.0010		0		5.773		0
Sum of Square									0.00662
combined uncertainty (Root of sum square)									0.08
Expanded Uncertainty (U, k=2)									0.16
% U									0.15

5. CONCLUSION

The secondary method for measuring electrolytic conductivity using Jones cell-type D has been established and validated with good accuracy and repeatability. As the characteristic of the measurement cell, the developed method can be employed in the 20-150 mS/cm region. This validated method has been successfully applied to assigning electrolytic conductivity values for secondary reference materials made by the Electrochemical Laboratory of SNSU-BSN, namely KCl 1 M (111.6 mS/cm with a relative expanded uncertainty of 0.15%), which are traceable to SI via a primary reference material from DFM Denmark. Hence, the secondary method can be a new approach for metrological dissemination in electrolytic conductivity measurement in Indonesia, including providing certified reference materials for testing laboratories.

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