Applicable Measuring Range of Two-Electrode Type Commercial Electrolytic Conductivity Meter for Accurate Determination of Electrolytic Conductivity

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Applicable measuring range of electrolytic conductivity (EC) for commercially available two-electrode type EC meter was examined. The measurement error caused by a gap in ECs between the measurement sample and the standard solution was also evaluated. Seven potassium chloride (KCl) solutions including certified reference materials (CRMs) manufactured by the National Metrology Institute of Japan (NMIJ) were measured, and the cell constants observed for commercial EC meters as well as the effect of electrode polarization were compared in detail under strict temperature control. The effect of electrode polarization can be sufficiently small if the frequency is properly selected. In the case of KCl standard solution with concentrations of 0.1 mol kg\(^{-1}\) (1 S m\(^{-1}\)) or less, the obtained cell constants were almost identical to those of declared ones. However, in the case of KCl standard solution with concentrations of 0.5 mol kg\(^{-1}\) (5 S m\(^{-1}\)) or more, the obtained cell constants showed 2-10% higher than those of declared ones. From these results, the calibration by standard solution with closer EC to the measurement solution is especially important if about 1% accuracy of measurement by commercial EC meter is required in higher EC range such as 5 S m\(^{-1}\) or more.

1. Introduction

Electrolytic conductivity (EC) is a useful parameter to evaluate solution characteristics in wider areas such as food safety, power generation, production of semiconductors, and pharmaceutical products [1, 2]. Several international or national documents such as ISO, ASTM, and JIS have been issued for the measurement of EC [3–7]. In addition, the USP indicates the EC as a primary indicator for water purity [8, 9]. The value of the EC of the aqueous solution varies drastically depending on the composition, and a wide range of EC is measured depending on the situation to evaluate solution characteristics from ultrapure water of 5.5 μS m\(^{-1}\) to seawater of 5.3 S m\(^{-1}\).

The EC is calculated by measuring the solution resistance. A model in which two electrodes are placed at each edge of a cylindrical cell filled with a solution is considered.

The solution resistance \(R (\Omega)\) between the electrodes is expressed by the following [10]:

\[
R = \frac{\rho l}{A},
\]

where \(l (m)\) is the length of the solution between the electrodes, \(A (m^2)\) is the area of the electrode, and \(\rho (\Omega m)\) is the resistivity of the solution. The resistivity of the solution is dependent on both the solution composition and its temperature. EC, \(\kappa (S m^{-1})\), is defined as the reciprocal of resistivity and is expressed by the following:

\[
\kappa = \frac{1}{\rho} = \frac{1}{RA}.
\]
A cell constant, $K_{\text{cell}} (\text{m}^{-1})$, is defined by the geometrical parameter by the following:

$$K_{\text{cell}} = \frac{l}{A}. \quad (3)$$

EC is expressed by the following formula, using the cell constant and solution resistance.

$$K = \frac{K_{\text{cell}}}{R}. \quad (4)$$

As mentioned above, the EC can be determined by measuring the solution resistance ($R$), length ($l$), and electrode area ($A$).

The cell for the measurement of EC can be classified into two types, primary and secondary cells, in accordance with the method to determine their cell constant [11]. The primary cell is used for absolutely measurement of EC; therefore, its cell constant should be determined accurately by only its geometric parameters such as length ($l$) and cross-sectional area ($A$) of the solution in which the actual current is flowing.

Most of the EC meters commercially available are categorized as secondary type since accurate geometric parameters cannot be easily obtained due to their shape and size even though it is easy to use. Therefore, the EC meter requires a calibration, in order to determine its cell constant, using a standard solution (usually an aqueous potassium chloride (KCl) solution) whose EC is determined in advance. The cell constant of the EC meter sometimes varies by undesirable changes in the positions of the electrodes and/or chemical or mechanical modifications of the electrodes. Therefore, the EC meters commercially available require periodic calibration. In the case of periodic calibration, single-point calibration is normally carried out. The use of a standard solution with similar EC to the measurement solutions is ideal to achieve accurate EC measurement. The EC measurement without an ideal standard solution, whose EC shows a larger bias to the measurement solution, sometimes encounters some bias due to the mismatching of the measuring value of EC between the standard and the measurement solutions. It implies that the different cell constant seemed to be obtained by each standard solution with different values of EC. Normally, EC meters commercially available have their cell constant determined in advance. However, it is supposed that the matching of the measuring range between the standard solution and the measurement one is not always considered, and some measurement error is caused. These factors mentioned below are considered for measurement error which results in the gap in the ECs between the measurement sample and the standard solution.

The resistance of the cable is a factor for the measurement error. An EC meter measures the resistance of the solution including its measurement system. In the case of a two-electrode type EC meter commercially available, the sum of both the solution and the cable resistance is measured. The value of the resistance of the cable connecting the cell and the galvanometer is a range from 0.01 $\Omega$ order to 0.1 $\Omega$ order depending on its length. If the high EC solution is measured, the solution resistance is small (ca. 1 $\Omega$ order), and the effect of the cable resistance becomes relatively large.

The electrode polarization is another factor of measurement error. The measurement of solution resistance is performed in alternating current (AC) to reduce the effect of electrode polarization. The value of the apparent solution resistance measured using AC is drastically depending on the frequency. Therefore, in accurate EC measurement, the solution resistances are measured by several frequencies and calculated by their extrapolation. On the other hand, commercially available EC meters measure the solution resistance at a specific frequency, because it is required to measure quickly and update the EC result in real time. In this case, the effect of the electrode polarization cannot be reduced completely, and the measurement error might be observed for measurement solutions with different ECs.

It is supposed that the real cell constant (not calibrated one) is independent of the composition of sample solutions, since it is only determined by the geometric parameter of the EC cell. However, depending on the cell design, this assumption is not always guaranteed [2, 12]. Jones-type cell is a cell that designed its cell constant independent of EC of the solution. Various types of primary Jones-type cells have been designed and applied currently by national metrology institutes (NMIs) [13, 14].

In our previous study, we confirmed that the cell constant of our National Metrology Institute of Japan (NMIJ) secondary Jones-type cell (Figure 1(a)) obtained by calibration using the solutions from 0.1 S m$^{-1}$ to 10 S m$^{-1}$ was identical within ca. 0.5% expanded uncertainty [11]. According to the research from Asakai et al., an EC meter as a detector of an ion chromatography showed higher solution resistance (lower EC) than that of the actual value, especially in the measuring range of EC more than ca. 0.1 S m$^{-1}$ [11]. On the other hand, according to the research of Thirstrup et al., ECs obtained between the primary measurement system and commercial EC cells were almost identical in the measuring range from ultrapure water to ca. 0.1 S m$^{-1}$ [15].

In this study, we evaluated measurement error caused by the gap of the ECs between the measurement sample and the standard solution for commercial EC meters with two-electrode type EC cell, since it was widely used due to its simplicity. The two-electrode type EC cell is suitable for measuring EC of small amount sample and is used to

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**Figure 1:** Graphical image of (a) NMIJ secondary Jones-type cell and (b and c) commercially available electrolytic conductivity meters (ECMs). The electrodes of commercial cells are platinum black.
measure the EC of valuable reagents such as ionic liquids. We measured seven standard KCl solutions by two EC meters commercially available (ECM-1 and ECM-2; Figures 1(b) and 1(c)) and discussed measurement error caused by the gap of the ECs between the measurement sample and the standard solution.

2. Materials and Methods

2.1. Measuring Instruments. The LCR meter used in the present study was a type E4980A from Agilent Technologies (Santa Clara, CA, USA), and its AC resistance was calibrated by Japan Calibration Service System (JCSS). The expanded uncertainty of AC resistance was 0.05% ($k=2$; hereinafter, $k$ indicates a coverage factor) in the ranges of 10 $\Omega$ to 1 M$\Omega$ at both frequencies 400 Hz and 1 kHz. The LCR meter was connected to secondary Jones-type cell and commercial EC ones with Kelvin clip leads from Keysight (Santa Rosa, CA, USA).

The thermometer used was a type 1502A from Fluke Corporation (Everett, WA, USA), with a Pt 100 platinum resistance temperature probe. The temperature from the thermometer was also calibrated by JCSS, and its expanded uncertainty was 0.008 K ($k=2$).

An air-thermostatic box was self-made and located in an air-conditioned laboratory controlled at a target temperature of around 25°C. The temperature inside the air-thermostatic box was controlled by Lauda RP845C and kept at a range from 24.98°C to 25.02°C.

NMIJ secondary Jones-type cell used in this study was previously described [11]. This cell is constructed with a rigid geometry: The cell volume and the positions of the electrodes are rigidly fixed [11], and have two platinum electrodes (ca. 20 mm diameter), which were facing away ca. 10 cm. Two commercial EC meters CT-58101B (TOA-DKK, Tokyo, Japan) and 3552-10D (HORIBA, Kyoto, Japan) were used and referred to as ECM-1 and ECM-2, respectively. Both cells are traditional two-electrode type and for tabletop use. The cell constants declared for ECM-1 and ECM-2 are 100.4 m$^{-1}$ and 95.2 m$^{-1}$, respectively, and both measurable ranges are also declared from 0.1 mS m$^{-1}$ to 10 S m$^{-1}$ in their specifications as listed in Table 1.

Because the terminals of the commercial EC cells could not be connected to the LCR meter, the end of the cable was cut off and connected to the LCR meter with Kelvin clip leads. The aqueous solutions of KCl with different molarities as standard solutions (0.01 mol kg$^{-1}$, 0.1 mol kg$^{-1}$, and 1 mol kg$^{-1}$ of KCl aqueous solutions) which have ECs of ca. 0.01 S m$^{-1}$, ca. 1.0 S m$^{-1}$, and ca. 10 S m$^{-1}$ were NMIJ-certified reference materials (CRMs) 5123a05, 5122a03, and 5121a04, respectively [15]. The aqueous solutions of KCl with different molarities as additional standard solutions (0.001 mol kg$^{-1}$, 0.01 mol kg$^{-1}$, 0.5 mol kg$^{-1}$, and 3 mol kg$^{-1}$) which have ECs from ca. 0.01 S m$^{-1}$ to ca. 30 S m$^{-1}$ were gravimetrically prepared by dissolving potassium chloride in pure water. The ECs of four additional KCl solutions were determined by NMIJ

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**Table 1: The declared cell constant and measuring range of two electrolytic conductivity meters commercially available.**

<table>
<thead>
<tr>
<th>Declared property</th>
<th>ECM-1</th>
<th>ECM-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell constant</td>
<td>100.4 m$^{-1}$</td>
<td>95.2 m$^{-1}$</td>
</tr>
<tr>
<td>Measuring range</td>
<td>0.1 mS m$^{-1}$ to 10 S m$^{-1}$</td>
<td>0.1 mS m$^{-1}$ to 10 S m$^{-1}$</td>
</tr>
</tbody>
</table>
secondary Jones-type cell whose cell constant was determined by the above three NMIJ CRMs.

2.2. The Measurements Procedure. Due to the low thermal conductivity coefficient of air, the cell and the EC meters were placed in the air-thermostatic box for at least 12 h before the measurement to reach the required temperature (from 24.98°C to 25.02°C). The temperature inside the box was monitored by the inserted thermometer.

In order to observe the frequency dependence of EC measurements, AC measurement method like electrochemical impedance spectroscopy was used. Electrochemical impedance spectroscopy consists of an AC-voltage signal at different frequencies and is measuring both real and imaginary parts of the impedance at each frequency throughout the frequency sweep. Measurement data were obtained for a frequency \( f \) ranged from 20 Hz to 625 kHz. All measurements were performed in the air-thermostatic box.

3. Results and Discussion

The solution resistance is determined by the electrochemical impedance spectroscopy analysis with linear extrapolation. The commercial EC cells had a larger inductance component than that of NMIJ secondary Jones-type cell, and a clear increase in reactance was observed in the high-frequency region (above 10 kHz). The extrapolation method according to the Nyquist plot (reactance vs. resistance plot) at zero reactance is affected by the inductance component as shown in Figure 2. Thus, we plotted resistance as a function of inverse frequency \( 1/f \) and extrapolated the \( f \) to \( f \rightarrow \infty \) to measure solution resistances and determine the cell constants for both ECM-1 and ECM-2 (Figure 3). This extrapolation method was commonly used [16], and it was reported that the results obtained were identical between the flat platinum and black platinum electrodes [17]. \( R \) vs \( 1/f \) is not linear in the low-frequency range [18]. Therefore, the solution resistance was extrapolated using only the high-frequency region except for the region that becomes a semicircle in the Nyquist plot.

In order to investigate the relationship between the calibrated cell constants of EC meters (ECM-1 and ECM-2) and the standard solutions with different ECs, we evaluated their cell constants using seven KCl standard solutions. In order to investigate a broader range in detail, a secondary Jones-type cell calibrated with NMIJ CRMs was used as an indicator. The cell constant of NMIJ secondary Jones-type cell was considered to be identical in the wide range of seven KCl concentrations because the cable resistance is very small, and the shape was designed to obtain the real cell constant which was not dependent on different ECs of the standard solution. The cell constants are evaluated using three NMIJ CRMs, and obtained cell constants are shown in Figure 4. The bars in Figure 4 are expanded uncertainties \( (k = 2) \) which were estimated by the combination of the following uncertainties: resistances of the LCR meter \( (0.025\%) \), thermometer \( (0.08\%) \), measurement repeatability \( (less than 0.1\%) \), and the cell constant of NMIJ secondary Jones-type cell \( (0.28\%) \).

![Figure 2: The resistances measured obtained by linear extrapolation for two EC meters commercially available.](image-url)

### Table 2: The resistances measured obtained by linear extrapolation for two EC meters commercially available.

<table>
<thead>
<tr>
<th>Standard solution</th>
<th>ECM-1</th>
<th>ECM-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol/kg</td>
<td>Ω</td>
<td>Ω</td>
</tr>
<tr>
<td>0.001</td>
<td>6799</td>
<td>6463</td>
</tr>
<tr>
<td>0.005</td>
<td>1404</td>
<td>1334</td>
</tr>
<tr>
<td>0.01</td>
<td>710.8</td>
<td>676.3</td>
</tr>
<tr>
<td>0.1</td>
<td>78.35</td>
<td>74.51</td>
</tr>
<tr>
<td>0.5</td>
<td>17.74</td>
<td>16.88</td>
</tr>
<tr>
<td>1</td>
<td>9.501</td>
<td>9.115</td>
</tr>
<tr>
<td>3</td>
<td>3.890</td>
<td>3.796</td>
</tr>
</tbody>
</table>

Figure 5: The cell constants of (a) ECM-1 and (b) ECM-2 obtained by calibration using the seven KCl standard solutions. Open circles are calculated by measured solution resistance and open squares are calculated by measured resistance subtracted cable resistance. The calculated cable resistances were 0.25 Ω (ECM-1) and 0.37 Ω (ECM-2). The bars were expanded uncertainties \( (k = 2) \) which were estimated by the combination of the following uncertainties: resistances of the LCR meter \( (0.025\%) \), thermometer \( (0.008\%) \), measurement repeatability \( (less than 0.1\%) \), and the cell constant of NMIJ secondary Jones-type cell \( (0.28\%) \).
determined from three NMIJ CRMs. The ECs of four additional KCl solutions (0.001, 0.05, 0.5, and 3 mol kg$^{-1}$) were also determined by NMIJ secondary Jones-type cell with an averaged cell constant, believing that the cell constant was identical for little outside of the range of EC covered by NMIJ CRMs, and total seven ECs were used in the following experiments.

Figure 5 shows the results of cell constants which are calculated by extrapolating $f$ to $f \rightarrow 0$ coin $R$ vs. $1/f$ plot obtained from seven KCl solutions by both ECM-1 and ECM-2. The bars are expanded uncertainties ($k = 2$). Both commercially EC meters show identical cell constants in the range from 0.001 mol kg$^{-1}$ (ca. 0.01 S m$^{-1}$) to 0.1 mol kg$^{-1}$ (ca. 1 S m$^{-1}$), and the calculated cell constants are almost the same as their declared values, 95.2 m$^{-1}$ and 100.2 m$^{-1}$ as listed in Table 1. However, in the range from 0.5 mol kg$^{-1}$ (ca. 5 S m$^{-1}$) to 3.0 mol kg$^{-1}$ (ca. 30 S m$^{-1}$), 2-10% larger cell constants were obtained.

The source of this phenomenon may be attributed to cable resistance. Table 2 shows the resistances of the KCl solutions measured by commercial EC meters and calculated with the extrapolation. In the case of KCl concentrations higher than 1 mol kg$^{-1}$, the effect of cable resistance becomes significant since the resistance value is very small on the order of 1 $\Omega$. Assuming that the cell constants calculated by subtracting cable resistance from the values in Table 2 were almost identical for all KCl solutions, the cable resistance of the commercial ECM-1 is calculated to be 0.25 $\Omega$ and that of the ECM-2 is 0.37 $\Omega$. Figure 5 also shows corrected cell constants calculated by subtracting the cable resistances from the values in Table 2. From these calculations, the cable resistance could be one of the sources for larger deviated cell constants of commercial EC meters. However, the assumed cable resistance was a bit larger than expected from the only total cable length (ca. 1.5 m). It was considered that the effect of other factors (e.g., the circuit elements of the commercial EC meter or the change of real cell constant) were still present.

We also examined the effect of electrode polarization on solution resistance measurement for constant frequency. Usually, a commercially available EC meter measures the solution resistance at a constant frequency since it is required to measure quickly and update the EC result in real time. The EC meters select a frequency suitable for the measurement solution from several frequencies (e.g., 100 Hz for lower EC and 50 kHz for higher EC) to reduce the effect of electrode polarization. In order to compare the solution resistance between the measured at a constant frequency and the extrapolated from values measured at several frequencies, the difference between the measured resistance and the resistance calculated with extrapolating $f$ to $f \rightarrow 0$ coin $R$ vs. $1/f$ plot is described as a relative value as shown in Figure 6. When the concentration of KCl was less than 0.01 mol kg$^{-1}$, the difference between the measured results at around 1 kHz and the calculated ones from extrapolation was smaller than 0.5%, for both EC meters. When the concentration of KCl was more than 0.1 mol kg$^{-1}$ and less than 1.0 mol kg$^{-1}$, the difference between the measured results at around 50 kHz and the calculated results from extrapolation was smaller than 0.5%, too, for both EC meters. This indicates that the measurement error due to the polarization effect can be sufficiently small if the frequency is properly selected.

As shown in Figure 6(a), above 10 kHz, the relative resistances increase with an increase of frequency for KCl solutions more than 0.5 mol kg$^{-1}$. The slopes of the increases in relative value are different, but the slopes of the increases...
in actual resistances are identical regardless of the KCl concentration as shown in Figure 7. Therefore, it was considered that the increases in resistance came from the circuit elements of the commercial EC meter, neither the cell nor the solution. A similar trend is observed in the result of the EC-2 as shown in Figure 6(b), although not as much as in EC-1.

4. Conclusions
Applicable measuring range of EC for commercially available two-electrode type EC meter was examined, and the sources of measurement error caused by the gap of the ECs between the measurement sample and the standard solution were discussed in this study. In the case of KCl standard solution with concentrations of 0.1 mol kg⁻¹ (ca. 1 S m⁻¹) or less, the obtained cell constants were almost identical with respect to those declared in their specifications. However, in the case of KCl standard solution with concentrations of 0.5 mol kg⁻¹ (5 S m⁻¹) or more, the obtained cell constants showed 2-10% higher than those declared in their specifications. From these results, in the measurement of higher EC of 5 S m⁻¹ or more, the calibration by standard solution with closer EC with respect to the measurement solution is especially important if about 1% accuracy is required. The resistance from cable could be the one of sources for the bias observed in this study. In the case of measuring EC, which varies drastically depending on the situations such as a management of food and pharmaceutical factory production line, it is not recommended to measure both higher and lower ECs with a single EC meter, especially for higher EC, even though the specification of EC meters covers the measuring range.

Data Availability
All data for this study are available from the corresponding author on responsible request.

Conflicts of Interest
The authors declare that there is no conflict of interest regarding the publication of this paper.

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