The stability study of electrolytic conductivity synthetic wastewater

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Abstract. The accurate and traceable measurement of electrochemical parameters, such as electrolytic conductivity, in water environment is crucial for water quality monitoring. This can be achieved by the use of metrological traceable certified reference material produced according to ISO 17034. It requires stability test of the reference material candidate as part of the certification for a new reference material. This study is focused on monitoring of the stability of electrolytic conductivity synthetic wastewater, as an example of complex solution containing high concentration of ions. The stability study is focused on the material of the packaging bottle, the shelf-life duration and the high temperature representing a shipping condition. The results demonstrate that the electrolytic conductivity synthetic wastewater is stable for all the conditions tested, but the synthetic wastewater packaged in glass bottle has longer shelf-life. The results confirmed that the synthetic wastewater has potential to be developed as a certified reference material.

1. Introduction
Electrolytic conductivity is one of water quality standards that has been widely used in various field including monitoring of the aquatic environment. It measures of how well a solution conducting electricity or estimates the total concentration of ionized substance in an electrolyte solution [1, 2]. It has a symbol of \( \kappa \) with the unit of S m\(^{-1}\). The value of \( \kappa \) is obtained from a measurement of solution resistance \( R_s \) of a homogenous, isotropic electrolyte placed between electrodes in a conductivity cell under specified conditions [1]. The electrolytic conductivity value has a relationship with the total dissolved solid (TDS), which has a symbol of \( \gamma \) [3, 4]. The ratio between TDS and electrolytic conductivity, namely conversion factor \( (K) \), defines the concentration of ions indicating roughly the concentration of major ions and dissolved solids (non-conductive materials) in the water [3-5]. Therefore, the value of conversion factor can be different depending on the different waters.

For the routine measurement for electrolytic conductivity and/or TDS, a conductivity meter is an easy and simple instrument but it can produce an accurate and reliable result. This meter is equipped with a probe, usually handheld, having two electrodes inside. After the probe is placed in the liquid to be measured, the meter applies voltage between two electrodes inside the probe. Electrical resistance from the solution causes a drop-in voltage, which is read by the meter. The meter converts this reading to milli- or microSiemens per centimetre.

In order to get accurate and reliable results, it is necessary to calibrate the conductivity meter regularly using certified reference materials (CRM) with established traceability to the International System of Unit (SI). Metrological traceability of the measurement results is crucial to fulfil the legal
requirement and to ensure the required measurement correctness with consideration to the expanded measurement uncertainty [6, 7]. Besides using traceable CRM, metrological traceability can also be ensured by taking part in an interlaboratory comparison, such as bilateral comparison or key comparison [6].

The needs for new CRMs are growing and become more specific as laboratories raise their awareness. This emphasises on how representative the reference materials are. ISO 17034:2016 describes the requirements for CRMs production including the assessments required in order to certify a reference material into a CRM, such as assessment of homogeneity, stability and property values [8]. The homogeneity assessment includes the homogeneity in the final packaging and assessment of its contribution to the uncertainty. The stability assessment monitors the stability and its uncertainty due to the effect of storage and transportation, while the property value includes identification of contributions to uncertainty [8]. The specific guidance on technical issue of the assessment of homogeneity, stability and characterization for the certification of reference materials is explained in ISO Guide 35:2017 [9].

In the water environment, monitoring of industrial wastewater plays an essential role for environmental protection to ensure process efficiency and to verify final quality of the effluent before discharging the wastewater to the environment. Reliable results for determination of electrolytic conductivity in wastewater are important for checking the performance of industrial wastewater treatment and detecting possible sources of industrial contamination. It needs accurate and reliable analytical results as well as the use of CRMs in order to draw valid conclusions. The CRMs are used to achieve traceability in chemical measurement, to calibrate the instruments, to validate the methods, to monitor laboratory performance and to permit comparison of methods [10].

This study is focus on investigating the stability of synthetic wastewater, as part of the assessment of a reference materials candidate. Until now, there is lack of CRMs for electrolytic conductivity measurement in complex or matrix solution. The only CRMs matrices for electrolytic conductivity measurement is the one in bioethanol matrices [11]. Thus, this study is important as preliminary research in developing CRMs in synthetic wastewater matrix. For this purpose, the synthetic wastewater was designed mimicking the real wastewater but without any biological compound. The feasibility of this synthetic wastewater has been studied before confirming that this composition had an electrolytic conductivity value of 7.430 mS cm⁻¹ and a conversion factor of 0.58 which was relevant to the real wastewater [12]. In this study, the stability of the synthetic wastewater is further assessed by considering the effect of the container used to package the synthetic wastewater, the shelf-life or storage duration and the transport condition.

2. Experimental section

2.1. Materials
Sodium hydrogen carbonate (NaHCO₃), potassium chloride (KCl), sodium chloride (NaCl) and hydrogen chloride (HCl) were purchased from Merck. All the chemicals are reagent grade.

2.2. Methods
The synthetic wastewater was prepared from 60 mg of NaHCO₃, 14 mg of KCl, 92 mg of NaCl and 2 mL of HCl 3 % for 1000 mL solution, as studied before [12]. The solution was stirred overnight to homogenize the mixture before it was transferred into the clean and dry container. There are two types container used; clear glass screw-cap bottles and high-density polyethylene (HDPE) bottles. All containers were thoroughly cleaned prior using. Upon received, the bottles were rinsed using deionized water, filled with the deionized water and capped. These filled bottles were kept overnight before being emptied and dried at the drying oven for overnight. The synthetic wastewater was filled into the clean and dry bottles and then stored away from daylight at a room temperature. The stability of electrolytic conductivity wastewater was checked in both types of bottle used to storage the solution. The shelf-life was determined by measuring the electrolytic conductivity synthetic wastewater at 25 ºC for the storage duration of 0, 1, 3, 6, 9, 12, 18 and 24 months after the production date. The stability of electrolytic
conductivity synthetic wastewater was also tested at higher temperature (40 °C) representing the stability of the solution during shipping or other transportation condition.

The electrolytic conductivity was measured using conductivity meter LAQUA F-74BW (Horiba) which has been calibrated using certified reference materials (IDNRM-MC-2-002) produced by Chemical Metrology Laboratory with the conductivity value of 6.67 mS cm⁻¹ and uncertainty of 0.03 mS cm⁻¹ at 25 °C. This reference materials were traceable to International Standard through CRM 1603 produced by Danish National Metrology Institute (DFM).

### 3. Results and discussion

The synthetic wastewater used in this study would be developed for a reference material candidate thus the stability assessment was conducted according to ISO 17034:2016 by considering the effect of the container used to package the synthetic wastewater, the shelf-life and the transport condition. The synthetic wastewater contained conductive ions and it was prepared from sodium hydrogen carbonate, potassium chloride, sodium chloride and hydrogen chloride [12]. The hydrogen chloride was added into the mixture because it could suppress carbon dioxide dissociation which is crucial especially for low electrolytic conductivity [13]. This synthetic wastewater was designed mimicking the real industrial wastewater in the absence of microbial, pathogenic compound and inorganic toxic metal for the safety reason. The synthetic wastewater was also free form any organic and volatile substances to maintain the solution stability during certain period of time and prevent the unnecessary biofouling [14].

The synthetic wastewater, as reference material candidate, were designed and produced with the electrolytic conductivity value of 7.430 mS cm⁻¹. Two types of container, clear glass and HDPE bottles, were prepared to package the synthetic wastewater. The reference value for electrolytic conductivity synthetic wastewater stored in each type of container was then assigned, as presented in Table 1. It shows the reference value and the expanded uncertainty for electrolytic conductivity synthetic wastewater in each type of container was still in agreement with the designed electrolytic conductivity value. The expanded uncertainty was calculated by considering the sources of uncertainty.

| Container type | Reference value (mS cm⁻¹) ± expanded uncertainty (k=2) |
|----------------|----------------------------------------------------------|
| Glass bottle   | 7.431 ± 0.0037                                           |
| HDPE bottle    | 7.430 ± 0.0039                                           |

All bottles containing synthetic wastewater were stored at room temperature and protected from direct sunlight. The electrolytic conductivity synthetic wastewater in each type bottle was measured at 25 °C as a function of storage time (0, 1, 3, 6, 9, 12, 18 and 24 months), as presented in Figure 1. This figure includes horizontal dotted lines (blue lines in Figure 1) showing the expanded uncertainty ($U_{RM}$, $k=2$) assigned to the reference value of the electrolytic conductivity synthetic wastewater filled in the glass and HDPE bottle. Figure 1 shows that the electrolytic conductivity value for the synthetic wastewater packaged in glass and HDPE bottles is in between the reference value with its expanded uncertainty (inside the area of horizontal dotted lines). After 12 months of storage, the electrolytic conductivity value synthetic wastewater packaged in both types of bottle starts to increase closer the upper limit of expanded uncertainty assigned to its reference value. It could be affected by the instability of the electrolytic conductivity synthetic wastewater filled in the bottles. Therefore, based on the type of container used to store the synthetic wastewater, it confirms that both types of container are suitable for packaging of the synthetic wastewater because the electrolytic conductivity values are adequately stable during the testing period.
Figure 1. The electrolytic conductivity synthetic wastewater packaged in glass bottle (a) and HDPE bottle (b) in a function of time (0, 1, 3, 6, 9, 12, 18 and 24 months) measured at 25 °C. The red dots are the electrolytic conductivity value with the standard deviation as the error bars and the blue dotted line are the reference values with their expanded uncertainties (k=2).

The stability of electrolytic conductivity synthetic wastewater packaged in the glass and HDPE bottles as a function of time was also tested at the temperature of 40 °C. This temperature is considered representing the elevated temperature that potentially encountered during transportation. The stability during transportation can be influenced by some factors, such as temperature and type of transportation used. However, this study is only focused on the temperature during transportation. This result can be used as a recommendation for transporting the reference material packaged in certain type of container. The stability at the elevated temperature (40 °C) for both glass and HDPE bottles as a function of time is presented in Figure 2. Similar to Figure 1, this figure also includes horizontal dotted lines (blue lines in Figure 2) showing the expanded uncertainty ($U_{RM}$, k=2) assigned to the reference value of the electrolytic conductivity synthetic wastewater filled in the glass and HDPE bottles.
Figure 2. The electrolytic conductivity synthetic wastewater stored in glass bottle (a) and HDPE bottle (b) in a function of time (0, 1, 3, 6, 9, 12, 18, and 24 months) measured at 40 °C. The red dots are the electrolytic conductivity value with the standard deviation as the error bars and the blue dotted lines are the reference values with their expanded uncertainties (k=2).

The electrolytic conductivity value for the synthetic wastewater packaged in both type of bottles and measured at elevated temperature has a different trend with the electrolytic conductivity synthetic wastewater measured at 25 °C. As shown in Figure 2, not all of the reference values of electrolytic conductivity (red dots) are in between the area of the reference value and its expanded uncertainty (blue dotted lines). When measured at 40 °C, the synthetic wastewater packaged in the glass and HDPE bottle have the electrolytic conductivity value above the reference value and its expanded uncertainty after 24 months and 18 months of storage, respectively. It shows that the synthetic wastewater at the elevated temperature would have longer shelf-life if packaged in the glass bottle than the one packaged in the HDPE bottle confirming the glass bottle is a more ideal container for packaging the reference material of the electrolytic conductivity.

Figure 3 summarises the percentage of the relative change in electrolytic conductivity synthetic wastewater over the time at different temperature and packaging container.
Figure 3. Relative change in electrolytic conductivity synthetic wastewater as a function of time packaged in different container, glass bottle (blue traces) and HDPE bottle (red traces), and measured at different temperature, 25 °C (a) and 40 °C (b).

Figure 3 shows the effect of temperature in the electrolytic conductivity of the synthetic wastewater. In general, the relative change in the electrolytic conductivity measured at elevated temperature (Figure 3(b)) is higher compared to the electrolytic conductivity measured at room temperature (Figure 3(a)) confirming that temperature is a sensitive parameter in electrolytic conductivity measurement. According to the previous reported study, increasing one degree Celsius increases the conductivity value about 1.5 % up to 5 % \cite{13, 15}. When the electrolytic conductivity sample measured at 25 °C (Figure 3(a)), the relative change in electrolytic conductivity for the wastewater packaged in the glass and HDPE container is almost the same, until about 12 months shelf-life. However, at 40 °C (Figure 3(b)), the relative change in electrolytic conductivity for the wastewater stored in HDPE bottle is higher than the electrolytic conductivity of the wastewater packaged in glass bottle. It confirms that the glass container is a more ideal container for packaging the synthetic wastewater as a reference material candidate.

4. Conclusion
The stability study of electrolytic conductivity synthetic wastewater as a reference material candidate has successfully conducted according to ISO 17034:2016. The stability study was conducted in two types of container used as packaging of the synthesis wastewater; the clear glass screw-cap bottles and the HDPE bottles. The stability of electrolytic conductivity synthetic wastewater in both containers was
monitored for 24 months with the time interval of 0, 1, 3, 6, 9, 12, 18 and 24 months at two different temperature; 25 °C and 40 °C representing the storage and transport temperature, respectively. The results confirm that both types of container are suitable for using as reference material packaging but having different shelf-life. The reference material candidate stored in glass bottle has better stability in higher temperature compared to the reference material candidate stored in HDPE bottle. Therefore, it is recommended to use the glass bottle as the packaging container for the reference material of electrolytic conductivity.

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