THE EFFECT OF PACKAGING TYPE AND STORAGE TEMPERATURE ON THE SHORT TERM STABILITY OF ELECTROLYTIC CONDUCTIVITY REFERENCE MATERIALS

AYU HINDAYANI[1], OMAN ZUAS*[1], NURYATINI HAMIM[1]

[1]Chemical Metrology, Centre for Research and Human Resources Development (PUSRISBANG), National Standardization Agency of Indonesia (BSN), Kawasan PUSPIPTEK SNSU Building 420, Serpong 15314, Tangerang Selatan - Banten, Indonesia

Abstract: In this work, monitoring the effect of packaging type and storage temperature on the short term stability of calibration standard solution KCl 1 M were conducted. The KCl 1M were packaged in two types of packaging i.e., high-density polyethylene (HDPE) and glass bottle. The effects of packaging type and storage temperature were monitored for four weeks at 25 °C and 40 °C. The conductivity values of KCl 1 M in the HDPE and glass bottle were 111.61 mS/cm and 111.62 mS/cm, respectively. The results indicated that the KCl 1M solution at 25 °C in both HDPE and glass bottle were found to be good in short term stability and there was no significant different between the two packaging types. At temperature of 40 °C, however, short term stability of the KCl 1 M in a glass bottle was better than the HDPE bottle.

Keywords: chemical metrology, calibration, homogeneity, primary standard solution, traceability.

1. INTRODUCTION

Reference material (or RM in short) refers to sufficiently homogeneous and stable materials with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process [1]. The RM plays an important role in the quality control of measurements, especially for validation of methods, instrument calibration, and estimation of uncertainty [2]. Several types of RM may include a pure substance, standard solution, gas mixtures, matrix RM and physico-chemical RM with their specific intended use [3]. The RM are also classified based on their measurement method and it may include primary, secondary, and in-house RM. The primary RM refers to any RM measured by the primary method and directly traceable to the International System of Units (SI). The secondary RM is defined as the RM that measured by the secondary method and traceable to primary RM. While in-house or working RM is an RM that is measured by the working method and traceable to secondary RM [2].

In Indonesia, the availability of RM is available with a very limited number. General speaking, the RM is only available from overseas countries by importing them and it is costly and time-consuming. In such a condition, therefore, developing and producing the RM at the local level becomes very important and can be an alternative to address the local needs. Electrochemistry laboratory as part of chemical metrology Indonesia has started to be developed the production of RM, especially in electrolytic conductivity (or EC in short) measurement in the range of 111 mS/cm. The RM was prepared from KCl 1 M solution and traceable to National Metrology of Denmark

*Correspondence author: oman@bsn.go.id

(DFM, Danish Fundamental Metrology). This RM can be used as a standard solution to calibrate the conductivity meter in monitoring the quality of seawater [4].

The EC value of KCl 1 M that produced by electrochemistry laboratory was measured by the secondary method using Jones Cell type D. Before used as a standard solution, the RM of KCl 1 M must be ensured for their homogeneity and stability as required in ISO 17034:2016 [5]. The stability of RM depends on the suitability of the packaging [6]. The stability of packaging for the RM solution (KCl) has been studied before, showing that a sealed ampoule is the most suitable packaging for EC RM [7]. But this type of packaging has disadvantages because a risk for substance to be contaminated with glass particles when the ampoules are opened [8].

Therefore, in this work, the stability of RM is evaluated by monitoring the effect of the type of packaging (HDPE and glass bottle) and storage temperature (at 25 °C and 40 °C) for four weeks that specifies the duration and condition of transportation the RM to the end-user in Indonesia.

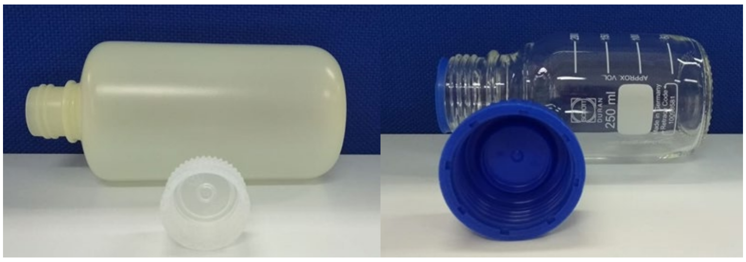
2. EXPERIMENTAL SETUP

2.1. Materials

Potassium chloride (KCl analysis grade, 99.5 % purity with molar mass 74.55 g/mol) was purchased from Merck, Germany. A CRM of the Primary standard solution with EC value 100 mS/cm at 25 °C (code CRM1714) was purchased from DFM. Demineralized water 0.055 μS/cm was produced from Thermo Scientific Barnstead Smart2pure water purification system used in all experimental runs.

2.2. Preparation of RM solution

One batch of RM solution was prepared from 1 M of KCl. The preparation procedure was adopted from literature [9]. The procedure was repeated for 14 times with an approximate total volume of 28 L. Then the solution was divided into 56 bottles of Nalgene^{TM} Narrow-Mouth HDPE bottle (Figure 1a) and 56 bottles of DURAN® glass bottle with screw-capand pouring ring (PP, blue) (Figure 1b) with volume 250 mL of each bottle. The EC value of KCl 1 M solution of each packaging was measured by the secondary method using Jones Cell type D. A statistical t-test was used to evaluate the significant difference of EC values for the two types of packaging. The EC values of the two types of packaging is no significant difference if $t_{stat} < t_{critical}$[10].



(a) (b)

Fig. 1. a) Nalgene^{TM} Narrow-Mouth HDPE bottle, b) DURAN® glass bottle with screw cap and pouring ring (PP, blue).

2.3. Procedure of EC measurement

The measurement of the EC value of RM for KCl 1 M solution in HDPE and glass bottles were conducted by the secondary method. The systems for secondary method are depicted in Figure 2. This system was equipped with a cell D (purchased from ZMK, Germany). The cell D is a glass tube with two platinization electrodes having diameter of 20 mm and the distance of the two electrodes is 60 mm. This cell has a cover plate, made from metal and grips to set the cell into the thermostatic bath (water bath Proline PV36 and Chiller DLK25, Lauda Germany) [11]. The temperature of measurement was measured using MKT50, Anton Paar Germany. The resistance of the RM for KCl 1 M solution was measured using a precision LCR meter (8105G, GW-Instek Taiwan). The detailed of procedure was adopted from literature [9].

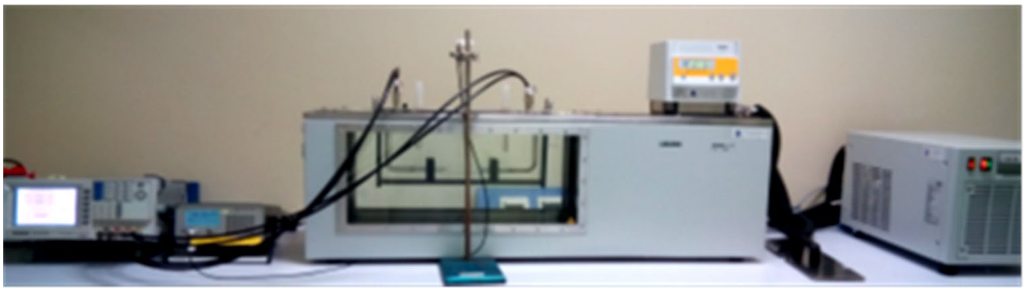


Fig. 2. The secondary EC measurement system [9].

Before calculating the EC value (κ) of RM for KCl 1 M, the cell constant (K_{cell}) of Jones cell type D must firstly be determined. This is in accordance with equation (1) [12].

$$κ = K_{cell} \times G \quad (1)$$

where G in mS is conductance that reciprocal of the resistance (R) in ohm (Ω) that described in equation (2) [13].

$$G = \frac{1}{R} \quad (2)$$

The cell constant is a factor for converting the measured conductance to conductivity [14]. Each cell has a different dimension of the electrodes. Therefore, each cell has a different cell constant that will be used in a different area of EC measurement [15]. In a secondary method, the cell constant is determined using a primary standard solution that traceable to SI [16]. In this study, CRM1714 from DFM was used as a primary standard solution. Therefore, this measurement is traceable to DFM. The cell constant (K_{cell}) in cm^{-1} was calculated using equation (3) [17].

$$K_{cell} = \frac{κ}{G} \quad (3)$$

where κ is the EC value of CRM1714 from the certificate (100 mS/cm) [18].

2.4. Homogeneity test

After the preparation, the RM of KCl 1 M solution was evaluated for its homogeneity. It is important to verify that all bottles of RM for KCl 1 M solution may identic with the same EC value [19]. In this homogeneity test, the EC value of RM for KCl 1 M solution was determined by measuring the KCl 1 M in both packaging types (HDPE and glass bottles) using Jones Cell type D with 10 bottles for each that randomly selected. Each measurement was conducted in two replicates. The F-test using a one-way analysis of variance (ANOVA) was then used to check the homogeneity of the RM for KCl 1 M solution. The RM is categorized as a homogenous solution if the value of $F < F_{critical}$ [12].

2.5. Effect of packaging types and temperature condition on the short-term stability

Eight bottles of HDPE containing 250 ml of RM for KCl 1 M solution were randomly selected and stored at 25 °C for 4 weeks. And, other 8 bottles of HDPE containing 250 mL of RM for KCl 1 M solution were stored at 40 °C for 4 weeks. Every week, the stability of the RM for KCl 1 M solution was monitored by measuring the KCl 1 M solution in HDPE bottles (2 bottles per week). The stability of the RM for the KCl 1 M solution was evaluated using linear regression analysis. The RM is categorized as stable if P-value for X Variable 1 more than 0.05 [12, 20, 21]. In a similar procedure, the stability of RM for KCl 1 M solution in a glass bottle was also measured and the result is reported.

3. RESULTS AND DISCUSSION

3.1. RM of KCl 1 M

The KCl 1 M solution is a common EC standard solution for the calibration of the conductivity meter with a value of 111 mS/cm at 25 °C [22]. The KCI solution is a very stable salt and it has been recognized as an international calibration standard for conductivity measurement [23]. In this work, the RM of KCl 1 M was in-house prepared at electrochemistry laboratory by keeping its traceable properties for end-user laboratories in Indonesia. Before determining the EC value of KCl 1 M, the cell constant of Jones Cell type D must be determined first to ensure the value of cell constant that will be used as a factor to calculate the EC value of KCl 1 M [14]. The measurement result for the calculation of the cell constant of Jones Cell type D are tabulated in Table 1 [9]. From Table 1, it can be seen that the cell constant of Jones Cell type D is 1.5167 cm^{-1}. Then, this cell constant was used to calculate the EC value of RM for KCl 1 M. The RM of KCl 1 M is very important for any laboratory to keep their EC measurement traceable to the SI unit and to assure reliable and precise measurement results [24]. In addition, to keep its traceable to the SI unit, ISO 17034:2016 [5] requires that the RM should also show good homogeneity and stability properties.

Table 1. Result measurement for the calculation the cell constant.

f (Hz)	1/f (Hz^{-1})	Resistance (Ω)
120	0.0083	15.1788
130	0.0077	15.1779
140	0.0071	15.1771
150	0.0067	15.1764
160	0.0063	15.1759
170	0.0059	15.1754
200	0.0050	15.1741
210	0.0048	15.1737
330	0.0030	15.1715
360	0.0028	15.1707
480	0.0021	15.1696
Intercept value	(Ω)	15.1668
Conductance (G) using Eq. (2)	(S)	0.0659
	(mS)	65.9335
EC value of CRM1714 from certificate (κ)	(mS/cm)	100
Cell Constant (K_{cell}) using Eq. (3)	(cm^{-1})	1.5167

3.2. Homogeneity test

It has been worldwide recognized that the homogeneity testing is a very important step to verify that all bottles as the packaging of RM solution have identical properties and to ensure that RM delivered to the end user laboratories are the same nominal value [25]. Thus, the RM of KCl 1 M is evaluated for its homogeneity before used. The homogeneity of the RM for KCl 1 M in both HDPE and glass bottles were tested and the testing results were used as the assigned value for RM of KCl 1 M. Table 2 and Table 4 list the measurement result of EC values for KCl 1 M in glass and HDPE bottles.

Table 2. Result measurements of EC value for KCl 1 M in glass bottles.

Number of Bottle	Result of Measurement, (mS/cm)		Average Value (mS/cm)
	1	2	
16	111.63	111.65	111.64
39	111.61	111.63	111.62
35	111.61	111.62	111.61
24	111.61	111.60	111.61
03	111.61	111.62	111.61
47	111.61	111.62	111.61
22	111.61	111.61	111.61
52	111.62	111.61	111.61
30	111.60	111.62	111.61
55	111.60	111.62	111.61
The assigned value for KCl 1 M in a glass bottle	111.62 mS/cm		

From Table 2, it can be seen that the assigned value for RM of KCl 1 M in a glass bottle is found to be 111.62mS/cm. Moreover, the homogeneity of KCl 1 M was evaluated by F-test using one-way ANOVA from 10 bottles that have been randomly selected. The results are listed in Table 3. From the statistical calculation, it can be observed that the value of F (3.019815) is less than of $F_{critical}$ (4.413873), indicating that the RM of KCl 1 M in the glass bottles are homogenous [12].

Table 3. One-way ANOVA of homogeneity testing for RM of KCl 1 M in glass bottle.

Source of Variation	SS	df	MS	F	P-value	$F_{critical}$
Between Groups	0.000337	1	0.000337	3.019815	0.099331	4.413873
Within Groups	0.002011	18	0.000112			
Total	0.002349	19				

Furthermore, the homogeneity testing of RM for KCl 1 M in the HDPE bottle was also conducted using the same procedure with glass bottles as mentioned above. Several bottles (10 bottles) of HDPE bottle containing KCl 1 M was randomly selected and measured and then results of EC values for KCl 1 M in HDPE bottles are shown in Table 4. From Table 4, it is known that the assigned value for KCl 1 M in HDPE bottle is 111.61 mS/cm. An F-test using one-way ANOVA against 10 HDPE bottles containing KCl 1 M was conducted for checking the homogeneity and the results are listed in Table 5. From Table 5, it can be observed that the value of F (0.296635) is less than $F_{critical}$ (4.413873). This result implies that the KCl 1 M in HDPE bottles is homogenous [12].

From the studies, it was found that the assigned value of KCl 1 M in both HDPE and glass bottles are 111.61 mS/cm and 111.62 mS/cm, respectively. Then, the possible statistical difference between these two assigned values was assessed by using a t-test. The results of the t-test for the EC value of KCl 1 M in both packaging types are shown in Table 6. It can be clearly seen that the two values having a very small difference. However, the t-test is required to determine for any significant difference between the means of the two group [26]. Table 6 shows that the t_{stat} (1.39) is less than $t_{critical}$ (2.26), implying the EC value of the two types of packaging is not statistically significantly different [27]. In addition, the statistical test indicates that one batch of KCl 1 M solution in both HDPE and glass bottle has a good homogeneity property.

Table 4. Result measurements of EC value for KCl 1 M in HDPE bottles.

Number of Bottle	Result of Measurement (mS/cm)		Average Value (mS/cm)
	1	2	
18	111.59	111.59	111.59
25	111.59	111.61	111.60
4	111.61	111.60	111.61
50	111.61	111.61	111.61
44	111.60	111.62	111.61
54	111.63	111.63	111.63
29	111.61	111.60	111.61
11	111.61	111.61	111.61
37	111.61	111.61	111.61
22	111.61	111.61	111.61
The assigned value for KCl 1 M in HDPE bottle	111.61 mS/cm		

Table 5. One-way ANOVA of homogeneity testing for KCl 1 M in HDPE bottles.

Source of Variation	SS	df	MS	F	P-value	$F_{critical}$
Between Groups	3.03E-05	1	3.03E-05	0.296635	0.592684	4.413873
Within Groups	0.001841	18	0.000102			
Total	0.001872	19				

Table 6. The t-test of EC values for KCl 1 M in HDPE and glass bottles.

	Glass bottles	HDPE bottles
Mean	111.62	111.61
Variance	8.17E-05	7.59E-05
Observations	10	10
Hypothesized Mean Difference	0	
df	9	
t_{stat}	1.39	
$t_{critical}$	2.26	

3.3. Stability test

The RM should not only have a good homogeneity property but also should sufficiently stable [28]. Stability is one of the key features of all RM. It is important that the value for each bottle of RM at the time of use is consistent with the stated value in the product certificate because the value of RM can change over time with various reasons [29]. Therefore stability testing is important way to determine the degree of instability of the RM after preparation and to confirm the stability of the material during storage, transportation and laboratory handling [6, 29]. There are two types of stability tests for RM i.e., long term and short-term stability. The long term stability is stability of RM during the period of validity under specified storage condition and short term stability is stability during transportation when RM is delivered to the customer [29]. In this work, the short term stability of RM for KCl 1 M was conducted for two types of packaging (i.e. HDPE and glass bottle), then at different temperature conditions (i.e. 25°C and 40°C) for 4 weeks. The results of EC measurement for KCl 1 M in a glass bottle at storage temperature of 40°C are shown in Table 7. Then, a regression analysis was used to evaluate the stability of KC1 1 M and the results are listed in Table 8.

Table 7. EC measurement of KCl 1 M in glass bottle that stored at 40 °C.

Week	Result of EC measurement, (mS/cm)
0	111.62
1	111.61
2	111.62
3	111.63
4	111.61

Table 8. Regression analysis of KC1 1 M in glass bottle that stored at 40 °C.

	Coefficients	Standard Error	t-stat	P-value
Intercept	111.618	0.007483315	14915.58	6.65E-13
X Variable 1	-1.42134E-15	0.00305505	-4.7E-13	1

From Table 8 can be observed that the P-value for X variable 1 (1) is higher than 0.05. It can be said that RM of KCl 1 M in a glass bottle is stable at 40°C for 4 weeks [12, 20, 21]. It is because the glass bottle is made from borosilicate that has highly inert, high chemical resistance, inert behavior at high temperatures up to 500°C [30]. Therefore there is no reaction of KCl 1 M in the glass bottle at 40°C and makes this solution stable. Then the EC measurement for RM of KCl 1 M in a glass bottle that stored at 25°C is tabulated in Table 9. Then, a regression analysis results for KCl 1 M in glass bottles stored at 25°C is listed in Table 10.

Table 9. EC measurement of KCl 1 M in glass bottle that stored at 25°C.

Week	Result of EC measurement, (mS/cm)
0	111.62
1	111.61
2	111.62
3	111.61
4	111.61

Table 10. Regression analysis of KC1 1 M in glass bottle that stored at 25°C.

	Coefficients	Standard Error	t-stat	P-value
Intercept	111.618	0.004	27904.5	1.01E-13
X Variable 1	-0.002	0.001632993	-1.22474	0.308068

From Table 10, it can be seen that P-value for X variable 1 (0.308068) is higher than 0.05. This value indicates that RM of KCl 1 M in glass bottles is stable at 25°C for 4 weeks. Then, the stability of KCl 1 M in HDPE bottles was evaluated its stability at 40°C and 25°C for 4 weeks. The EC measured values for KCl 1 M in HDPE bottles at 40°C are listed in Table 11.

Table 11. EC measurement of KCl 1 M in HDPE bottle that stored at 40 °C.

Week	Result of EC measurement, (mS/cm)
0	111.61
1	111.62

2	111.62
3	111.63
4	111.63

It can be seen from Table 11 that the EC values increase with time. In this regard, stability is required to be evaluated by using regression analysis. This evaluation is aimed to ensure the stability property of the KCl 1 M solution since increasing the EC value (Table 11) is questionable. The results of regression analysis are listed in Table 12.

.

Table 12. Regression analysis of KC1 1 M in HDPE bottle that stored at 40 °C.

	Coefficients	Standard Error	t-stat	P-value
Intercept	111.612	0.002449	45565.41	2.33E-14
X Variable 1	0.005	0.001	5	0.015392

From Table 12, it can evidence that P-value for X variable 1 (0.015392) is less than 0.05. It is indicated that the RM of KCl 1 M in HDPE bottles is unstable at 40°C for 4 weeks. The instability might be caused by the evaporation of KCl solution at 40°C or leaching of the HDPE bottles. Evaporation occurs through the space between the bottle and the cap, usually resulting from the cap relaxing and loosening with time. Leaching of ions from the container or reactions of the solution with the container may also occur. All these effects cause the solutions of KCl unstable. This result is in agreement with a previous study [31] because evaporating and leaching may cause the conductivity of the solution lead to increase with time. Then, the results of EC measurement values for stability study of KCl 1 M in HDPE bottles at 25°C are shown in Table 13. Then, a regression analysis results for KCl 1 M in HDPE bottles stored at 25°C is listed in Table 14.

Table 13. EC measurement of KCl 1 M in HDPE bottle that stored at 25 °C.

Week	Result of EC measurement, (mS/cm)
0	111.61
1	111.61
2	111.61
3	111.61
4	111.60

Table 14. Regression analysis of KC1 1 M in HDPE bottle that stored at 25 °C.

	Coefficients	Standard Error	t-stat	P-value
Intercept	111.612	0.002828	39460.8	3.59E-14
X Variable 1	-0.002	0.001155	-1.73205	0.18169

From Table 14, the data indicates that the P-value for X variable 1 is 0.18169. This value is higher than 0.05. It is indicating that RM of KCl 1 M is stable when stored in 25°C for 4 weeks.

4. CONCLUSIONS

As much as 28 L of RM for KCl 1 M as a standard solution for calibration of the conductivity meter has been made by electrochemistry laboratory - chemical metrology Indonesia. This solution was homogenously packaged in HDPE and glass bottle, having conductivity values were 111.61 mS/cm and 111.62 mS/cm, respectively. It was stable when stored at 25°C. Then, the glass bottle was found to be the best packaging of KCl 1 M for transportation at 40°C for 4 weeks.

ACKNOWLEDGEMENTS

The authors express their sincere appreciation to the Research Centre for Metrology – Indonesian Institute of Sciences (LIPI) for funding this research and thanks to Centre for Research and Human Resources and Development – National Standardization Agency of Indonesia (PUSRISBANG SDM – BSN).

REFERENCES

[1] ISO Technical Committees, ISO Guide 30:2015 in reference materials — selected terms and definitions, ISO copyright, Switzerland, 2015.
[2] Eurachem, The selection and use of reference materials, in a basic guide for laboratories and accreditation bodies, Eurachem, Europe, 2002.
[3] EEE-RM Working Group., The selection and use of reference materials, European accreditation, Europe, 2003.
[4] Breuel, U., Werner, B., Jehnert, D., Metrology in chemistry for pH and electrolytic conductivity traceability dissemination, Chimia, vol. 63, 2009, p. 643-646.
[5] ISO Technical Committees., ISO 17034-general requirements for the competence of reference material producers, ISO copyright, Switzerland, 2016.
[6] Faure, U., Wagstaffe, P.J., Stability of reference materials, Fresenius journal of analytical chemistry, vol. 345, 1993, p. 124-126.
[7] Shreiner, R.H., Stability of standard electrolytic conductivity solutions in glass containers, Journal of research national institute of standards and technology, vol. 107, 2002, p. 393–399.
[8] WHO Expert Committee, Annex 3: general guidelines for the establishment, maintenance and distribution of chemical reference substances, Geneva, 2006.
[9] Hindayani, A., Zuas, O., Elishian, C., Aristiawan, Y., Hamim, N., Uncertainty estimation for the measurement of electrolytic conductivity by secondary method using cell type D, Periódico tchê química, vol. 16, 2019, p. 911-919.
[10] Kim, T.K., T test as a parametric statistic, Korean journal anesthesiology, vol. 68, 2015, p. 540-546.
[11] Breuel, U., Werner, B., Spitzer, P., Jensen, H.D., Experiences with novel secondary conductivity sensors within the german calibration service (DKD). NCSLI measure, vol. 3, 2008, p. 32-36.
[12] Fraga, I.C. S., Lopes, J.C., Sobral, S.P., Ribeiro, C.M., Certification of a low value electrolytic conductivity solution using traceable measurements, Accreditation and quality assurance, vol. 18, 2013, p. 99–104.
[13] Breuel, U., Garbotz, N., Werner, B., Experiences with novel secondary conductivity sensors within the German calibration service (DKD), NCSL International workshop and symposium, Saint Paul, Minnesota, 2007.
[14] Radiometer analytical SAS., Conductivity theory and practice, France, 2004.
[15] Slovacek, D., Measurement of conductivity, Hach Company, Loveland, 1998.
[16] Breuel, U., Werner, B., Spitzer, P., Jensen, H. D., Experiences with novel developed secondary conductivity sensors within the German calibration service (DKD), NCSL international workshop and symposium, 230th PTB Seminar conductivity and salinity, Braunschweigh, 2007.
[17] Wu, Y.C., Berezansky, P. A., Low electrolytic conductivity standards. Journal of research national institute of standards and technology, vol. 100, 1995, p. 521-527.
[18] Snedden, A., Certificate of analysis certified reference material reference solution of electrolytic conductivity 100 mS/cm, DFM, Denmark, 2017.
[19] Pauwels, J., Lamberty, A., Schimmel, H., Homogeneity testing of reference materials. Accreditation and quality assurance, vol. 3, 1998, p. 51-55.
[20] LGC, EU-Indonesia trade support programme II (TSP2): standard relating to setting up a reference material producers accreditation system-ISO Guide 35-stability study, England, 2013.
[21] De Souza, V., Rodrigues, J.M., Bandeira, R.D.C., Valente, L.A.N., Sousa, M.V.B., Da Silva, V.F., Da Silva, R.A.L., Evaluation of stability of ethanol in water certified reference material: measurement uncertainty under transport and storage conditions. Accreditation and quality assurance, vol. 13, 2008, p. 717-721.
[22] OIML, OIML R 56: standard solutions reproducing the conductivity of electrolytes, Bureau international de metrologie legale, Prancis, 1981.
[23] DB Water Technologies., KCl standard solution, https://www.glycolfeeder.com/searchresults.asp?cat=43, Accessed 14/01/2019.
[24] Brinkmann, F., Dam, N.E., Deak, E., Durbiano, F., Ferrara, E., Fükü, J., Jensen, H. D., Mariassy, M., Shreiner, R.H., Spitzer, P., Sudmeier, U., Surdu, M., Vyskocil, L., Primary methods for the measurement of electrolytic conductivity, Accreditation and quality assurance, vol. 8, 2003, p. 346–353.
[25] Quevauviller, P., Requirements for production and use of certified reference materials for speciation analysis: a european commission perspective, Spectrochimica acta, part B, vol. 53, 1998, p. 1261–1279.
[26] Investopedia, T-test, https://www.investopedia.com/terms/t/t-test.asp, Accessed 14/01/2019.
[27] Minitab., Using the t-value to determine whether to reject the null hypothesis, https://support.minitab.com/en-us/minitab-express/1/help-and-how-to/modeling-statistics/regression/supporting-topics/regression-models/using-the-t-value-to-determine-whether-to-reject-the-null-hypothesis/, Accessed 14/01/2019.

[28] Van der Veen, A.M.H., Linsinger, T.P.J., Lamberty, A., Pauwels, J., Uncertainty calculations in the certification of reference materials: 3. stability study, Accreditation and quality assurance, vol. 6, 2001, p. 257-263.
[29] ISO Technical Committees, ISO Guide 35:2017 in reference materials – guidance for characterization and assessment of homogeneity and stability, ISO copyright, Switzerland, 2017.
[30] Schoot Duran, Laboratory glass bottles and screw caps, https://www.schott.com/d/uk/c260afa3-294c-41ee-a7eb-1855e88cdfee/1.0/bottles_caps.pdf, Accessed 10/01/2019.
[31] Shreiner, R.H., Pratt, K.W., Standard reference materials: primary standards and standard reference materials for electrolytic conductivity, NIST special publication 260-142, Washington, 2004.