CRM REPORT

A C G publications

J. Chem. Metrol. XX:X (2025) X-XX

journal of chemical metrology

Development of a quality control material for conductivity measurements in food and environmental applications

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(Received August 10, 2025; Revised August 28, 2025; Accepted September 01, 2025)

Abstract: The accuracy and reliability of conductivity measurements in analytical laboratories depend significantly on the availability of quality control materials. This study addresses the preparation, homogeneity, stability and characterization of a potassium chloride (KCl) quality control material (QCM) of 1414 µS/cm based on ISO/TR 33402. OIML R-56 does not contain this conductivity value as a secondary standard, so the mass of KCl required to prepare such a solution was experimentally defined. The conductivity measurements were carried out at 25 °C using a conductivity meter calibrated by a CRM produced by the the Slovak Institute of Metrology (SMU), a signatory to the mutual recognition arrangement (MRA) of the International Committee of Weights and Measures (CIPM). The homogeneity study was carried out in accordance with ISO 33405 using 10% of the batch bottles and the analysis of variance (ANOVA) showed that the QCM batch is homogeneous. The short-term stability was carried out over 4 weeks storage time at 4°C and 40°C and the isochronous measurements showed no significant deviations over time. The characterization of the QCM along three days showed that, its conductivity was 1414.11 µS/cm. The uncertainty associated with the conductivity measurements was assessed based on the requirements of the Guide to the expression of uncertainty in measurement (ISO GUM) and the EURACHEM/CITAC Guide, CG4 (Quantifying uncertainty in analytical measurement). It was found to be 23.10 µS/cm or 1.63%. A control chart was developed using the prepared QCM and the measured values remained within the control limits over the control time of six weeks. The prepared KCl QCM will be useful for use in quality control and instrumental validation in food, drug and environmental conductivity testing.

Keywords: Conductivity; QCM; ISO/TR 33402; homogeneity; stability; control chart.

1. Introduction

Electrical conductivity (EC) is one of the most frequently measured water quality parameters. It has been used to assess the salinity, ionic strength, major solute concentrations and total dissolved solids of natural waters and soil solutions [1-3]. Pure water exhibits very low conductivity (~0.055 µS/cm), whereas typical drinking water ranges between 200–800 µS/cm and seawater reach approximately 50000 µS/cm. Monitoring EC is crucial for detecting pollution events, evaluating treatment processes and ensuring compliance with regulatory standards [4,5].

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The article was published by ACG Publications
http://www.acgpubs.org/journal/journal-of-chemical-metrology Month-Month 2025 EISSN:1307-6183
DOI:http://doi.org/10.25135/jcm.119.2508.3607

Conductivity meters are the primary instruments used to measure EC in aqueous solutions. These devices function by applying an alternating current between electrodes immersed in the sample and measuring the resulting voltage, which correlates with the solution ability to conduct electricity. Modern conductivity meters offer features such as automatic temperature compensation and digital calibration, enhancing measurement accuracy and reliability. Their portability and ease of use make them indispensable tools for both field assessments and laboratory analyses [6-8]. Over recent years, significant advancements have been made in EC measurement techniques. Research has focused on improving sensor materials to reduce fouling, integrating EC measurements with other water quality parameters and developing automated monitoring systems for real time data acquisition. These innovations have expanded the applicability of EC measurements in various sectors, including environmental monitoring, agriculture and food safety [9-12]. Ensuring the quality of EC measurements necessitates good quality control (QC) practices. The development of quality control materials provides laboratories with reliable tools to assess instrument performance and detect systematic errors. These materials are essential for maintaining the integrity of analytical results across different testing scenarios [13,14]. ISO/TR 33402 provides comprehensive guidance on the selection and use of Quality Control Materials (QCMs) to support measurement quality in analytical laboratories [15]. The standard defines QCMs as materials used to monitor the performance of measurement systems and ensure the validity of test or calibration results. They are essential components of quality assurance, particularly in laboratories operating under ISO/IEC 17025. The primary purpose of QCMs is to assess the stability and reliability of analytical systems, detect performance trends or anomalies and support ongoing method validation. The QCMs are categorized into various types, including in-house prepared materials, commercially available products and non-certified reference materials, emphasizing that their selection should be based on fitness for purpose. Key requirements for QCMs include adequate homogeneity, stability over the intended use period and relevance to the matrix and concentration range of routine samples. Additionally, QCMs must be properly documented, including preparation protocols and handling instructions. The ISO/TR 33402 also provides recommendations on the appropriate characterization, labeling and implementation of QCMs within quality control procedures to ensure consistent measurement performance [15,16]. In this paper, we present the preparation, homogeneity, stability and characterization of a 1414 µS/cm conductivity solution intended for use as a QC material in environmental and food testing laboratories. Assessment of the quality control material homogeneity, stability in addition to the material characterization and uncertainty were carried out in accordance with the requirements of ISO 33405, ISO GUM and EURACHEM/CITAC Guide CG4 [17-19]. The intended QCM will be useful for a wide range of food and environmental analytical laboratories. Details of the preparation and the various measurements are described.

2. Experimental

2.1. Reagents

Potassium chloride (99.5-100.5%) was obtained from ARG, Germany. Ultrapure water used for preparation of the quality control material was obtained by Melbourne water purification system. The conductivity CRM of 1410.6±2.8 µS/cm used for calibration was obtained from SMU, Slovakia.

2.2. Equipment

An analytical balance with a weighing capacity of 220 g and a resolution of 0.01 mg, manufactured by Mettler Toledo, Switzerland was used for weighing KCl. A second balance with a weighing capacity of 60 kg and a resolution of 1 mg was used for weighing the QCM batch solution. The inoLab® Cond 7310 Conductivity Benchtop Meter was supplied by WTW, Germany with a special conductivity measuring cell TetraCon® 325-x | 4 electrodes | graphite. The mechanical shaker (model HS 501 D S000) was obtained from IKA, Germany. A water bath equipped with a calibrated thermostat was used to maintain a water medium at 25 °C for conductivity measurements. The temperature of measurements was measured by a calibrated thermometer. A clean grade A glass beaker was used to dissolve the weighed KCl for the batch preparation. The 10 L plastic container and the HDPE bottles were purchased from a local supplier.

2.3. The Preparation of the QCM Batch

Potassium chloride (KCl) was ignited at 420 °C for 4 hours, then allowed to cool in a desiccator before weighing. The precise mass of KCl required to prepare a 7.5 kg batch of QCM solution was determined experimentally and weighed into a clean beaker, corrected for air bouncy and fully dissolved in an ultrapure water. The dissolved mass was filtered using 0.45 µm PTFE, then transferred into a plastic container already containing approximately 2 kg of ultrapure water. The container was placed on a 60 kg capacity balance for accurate mass measurement. The solution was gently swirled to ensure homogeneity then, ultrapure water was added until the target solution mass was reached. The container was then tightly closed, swirled again and placed on a mechanical shaker overnight to ensure complete homogeneity of the QCM solution. The homogenized batch was distributed into 30 numbered 250 mL HDPE bottles, which were tightly closed and sealed.

2.4. Homogeneity, Characterization and Stability Study

For the homogeneity study, three bottles were systematically selected (B1, B15 and B30) and each bottle was subdivided into three parts. The conductivity of each part was measured twice in a random order within a single run, resulting in a total of six measurements per bottle. For the short-term stability study, nine bottles were selected from the QCM batch. Four were stored at 4 °C for 1, 2, 3 and 4 weeks respectively, while another four were stored at 40 °C for the same durations. One bottle was kept at ambient temperature (21 °C) for the entire four weeks period. Following storage, all samples were transferred to a reference temperature of 4 °C overnight and then equilibrated to room temperature prior to isochronous conductivity measurements at 25 °C. On the other hand, characterization of the QCM batch was performed using three selected bottles. Each bottle was measured on three different days (D1–D3) with three measurements taken per day.

2.5. Conductivity Measurements

Before the measurements, the conductivity meter was calibrated at 25 °C using the certified reference material (CRM) 1410.6 µS/cm. The sample to be measured was placed in a beaker positioned in a water bath maintained at 25 °C and the conductivity electrode was immersed until a stable reading was obtained. The temperature was measured using a calibrated thermometer.

3. Results and Discussion

3.1. Defining the KCl Mass for a Solution of 1414 µS/cm

To prepare a quality control material of 1414 µS/cm in-house, reference was made to the international standard OIMLR 56:1981[20]. This standard provides three specific KCl masses expressed in g per 1000 g of H_2O along with their corresponding conductivity values in S/m at 25°C as secondary standards. These three conductivity values were converted to µS/cm and presented in Table 1.

Table 1. Conductivity of secondary standards at 25 °C

KCl (g/1000g H_2O)	S/m	µS/cm
0.37329	0.07182	718.2
0.14932	0.02916	291.6
0.07466	0.01469	146.9

As it can be seen from the table, a solution with a conductivity of 0.1414 S/m (or 1414µS/cm) is not listed. Therefore, an attempt was made to determine whether the KCl masses and their corresponding conductivities in Table 1 could be used to estimate the required mass for a solution with the desired conductivity of 1414µS/cm. For this purpose, Equation 1, which correlates each listed mass and conductivity with the target conductivity of 1414 µS/cm was applied,

$$m_2 = \frac{m_1 \times k_2}{k_1} \tag{1}$$

where,

m_2 - unknown mass of KCl (g) corresponding to 1414 µS/cm

k_2 - conductivity of 1414 µS/cm

m_1 - mass of KCl corresponding to conductivity value in OIML R 56

k_1 - the conductivity value corresponding to KCl mass in OIML R 56

Using this equation, three KCl masses were obtained: 0.73494 g, 0.72407 g and 0.71865 g. The variation among these values indicates that a single and definitive mass for preparing a solution of 1414 µS/cm cannot be directly derived from the OIML R 56 data. Therefore, it was decided to proceed with a series of experimental trials. Different KCl masses were used to prepare solutions and their conductivities were measured to identify the precise mass that would yield the target conductivity of 1414 µS/cm. To guide the experimental design, the molality (mol/kg) for each mass in Table 1 was calculated using Equation 2, where MW is the molecular weight of KCl.

$$m = \frac{m_1 \times p}{MW \times m_2} \tag{2}$$

where,

m - Molality of KCl (mol/kg)

m_1 - mass of KCl (g)

p - purity of KCl (%)

MW - molecular weight of KCl (g/mol)

m_2 - mass of solvent (kg)

The calculated molalities and their corresponding conductivities were recorded in Table 2. A linear

Table 2. The molality of the OIML R-56 KCl masses and the equivalent conductivity

Molality (mol/kg)	Conductivity (µS/cm)
0.005007	718.2
0.002003	291.6
0.001001	146.9

relationship between these molatity values and the corresponding conductivities was observed, yielding the equation: $y = 142476x + 5.0773$. Substituting $y = 1414$ into this equation, the corresponding molality (x) was found to be 0.00988 mol/kg, which was used as a starting point for preparing a series of KCl solutions with slightly varying concentrations to identify the molality that achieves a conductivity of 1414 µS/cm. The KCl mass required to prepare the 0.00988 mol/kg solution was calculated using Equation 3 and found to be 0.73669 g, but the actual mass used was 0.73760 g.

$$m = n_{x} MW \qquad (3)$$

The conductivity of that solution was measured 10 times yielding an average value of 1395.8 µS/cm as shown in Table 3, but this value is still below the target.

Table 3. The KCl mass and the measured conductivity of the three prepared solutions

Concentration (mol/kg)	0.00988	0.01000	0.01003
Target mass (g)	0.73669	0.74550	0.74774
Actual mass (g)	0.73760	0.74470	0.74770
Conductivity, µS/cm	1395	1407	1413
	1395	1406	1413
	1396	1406	1414
	1395	1407	1413
	1395	1407	1414
	1397	1407	1412
	1396	1407	1413
	1396	1408	1413
	1397	1407	1413
	1396	1407	1414
Average	1395.8	1406.9	1413.2
SD	0.79	0.57	0.63

To increase the conductivity, a slightly higher concentration of 0.01000 mol/kg was selected. The required KCl mass was calculated as 0.74550 g, but the actual mass used was 0.74470 g. Ten conductivity measurements were made, resulting in an average of 1406.9 µS/cm, which is closer to the target conductivity. Furthermore, a solution with a concentration of 0.01003 mol/kg was prepared and the calculated KCl mass for preparing it was 0.74774 g, while the actual mass used was 0.74770 g. Ten conductivity measurements were again performed and their average was 1413.2 µS/cm as reported in Table 3. This value is effectively close to the target value. Based on these experimental findings, it can be concluded that the optimal KCl mass required to prepare a standard conductivity solution with a value of approximately 1414 µS/cm is 0.74770g/1000g H_2O.

3.2. Homogeneity of the QCMs

The defined KCl mass of 0.74770g was multiplied by 7.5 to obtain 5.60775 g which is the mass required to prepare a QCM batch of 7.5 kg H_2O. The batch was dispensed into 30 bottles, each is 250 mL as described above. To evaluate the homogeneity of the quality control material (QCM), three bottles (B1, B15, and B30) representing 10% of the total batch were systematically selected for analysis [17,21]. Each bottle was subdivided into three portions and the conductivity of each portion was measured twice, resulting in six replicate measurements per bottle. The measurements were carried out by a conductivity meter at 25°C and the results, including the individual measurements, mean values and standard deviations are presented in Table 4.

Table 4. the homogeneity results of the selected QCM bottles.

	B1	**B15**	**B30**
Conductivity, µS/cm	1415	1414	1413
	1415	1414	1415
	1414	1415	1414
	1413	1414	1413
	1414	1414	1414
	1414	1413	1413
Ave	1414.17	1414.00	1413.67
SD	0.75	0.63	0.82

They were also graphically represented in Figure 1 in which the error bars represent the standard deviations of the means.

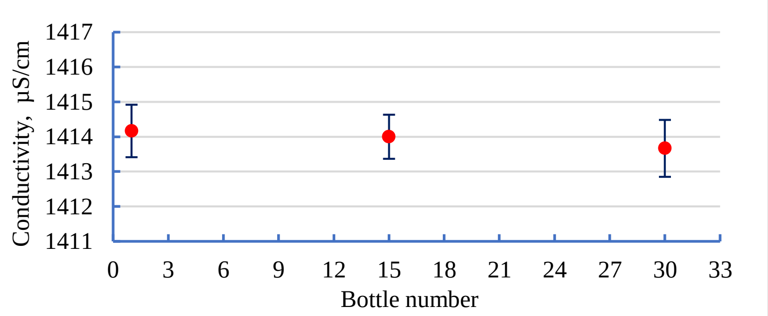

Figure 1. the bottle number used in homogeneity study versus conductivity

The conductivity values showed a very narrow range across the three bottles (1413.67 to 1414.17 µS/cm) with the maximum difference between bottle means not exceeding 0.5 µS/cm. Furthermore, the within bottle standard deviations were consistently below 1 µS/cm reflecting high repeatability and good measurement precision. To assess whether the observed differences between bottles were significant, a one-way analysis of variance (ANOVA) was conducted and the results were summarized in Table 5.

Table 5. One-way ANOVA results for conductivity measurements.

Source of Variation	**SS**	**df**	**MS**	**F**	**P-value**	**F crit**
Between Groups	0.77778	2	0.38889	0.714	0.51	3.682
Within Groups	8.16667	15	0.54444			
Total	8.94444	17				

The analysis yielded an F-value of 0.714, which is below the F-crit of 3.682 and a p-value of 0.51, which is well above the commonly accepted significance threshold of 0.05 [22,23]. These findings indicate that there is no statistically significant variation between the bottles and that the minor differences observed can be attributed to random variation inherent in the measurement process, rather than to any systematic inhomogeneity. Moreover, ISO guide 80 states that: to be of use as a QCM, the between bottle standard deviation should be no greater than one third of the within laboratory reproducibility standard deviation (which can be obtained from existing control chart data, where available or from existing reproducibility and repeatability data for the method). To investigate this criterion, the between bottle standard deviation was estimated using Equation 4, where *n* represents the number of replicates per bottle ($n = 6$). The calculated value was negative (-0.0258) and was interpreted as zero, which suggests that no measurable between-bottle variance exists beyond the expected analytical variability.

$$s_A = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \qquad (4)$$

The pooled within bottle standard deviation (s_{pooled}) was calculated using Equation 5 where S_1, S_2 and S_3 are the standard deviation for B1, B15 and B30 respectively.

$$s_{pooled} = \sqrt{\frac{(n_1-1)s_1^2 + (n_2-1)s_2^2 + (n_3-1)s_3^2}{n_1+n_2+n_3-3}} \qquad (5)$$

The s_{pooled} was found to be approximately 0.737 µS/cm, then the homogeneity threshold was calculated according to criterion mentioned above as: 1/3 *x* 0.737 and was found to be 0.22 µS/cm. Since the estimated between bottle variation (s_A) was effectively zero, it can be concluded that the QCM batch clearly meets this threshold. Taken together, the results of replicate measurements, ANOVA and comparison with the established threshold confirm that the quality control material exhibits a high degree of homogeneity.

3.3. Characterization of the QCMs

The characterization measurements were performed on three selected bottles (B2, B16 and B29) over three separate days. For each bottle, three replicate conductivity measurements were taken per day and the measurement results were reported in Table 6.

Table 6. the characterization results (µS/cm) of the QCMs in 3 days

Day	B 2	B 16	B 29
D 1	1413	1413	1413
	1413	1414	1413
	1413	1414	1413
D 2	1415	1415	1415
	1415	1415	1415
	1415	1415	1414
D 3	1413	1414	1415
	1414	1415	1414
	1414	1415	1414
Average	1413.89	1414.44	1414
SD	0.93	0.73	0.87
Grand Mean	1414.11		

The results were tested for outliers by Grubs test and no outliers were detected [24]. The average of the three days measured values was calculated for each bottle and the grand mean was then calculated from the individual bottle means. The results demonstrate a high level of consistency among the measurements, both across different bottles and on different days. The average values ranged from 1413.89 to 1414.44 µS/cm, with a small variation of just 0.55 µS/cm, which indicates a very good stability of the samples. The standard deviations (SD) for the three bottles were relatively low: 0.93 for B2, 0.73 for B16 and 0.87 for B29. These low SD values reflect good repeatability within each set of measurements and indicate that random error was kept to a minimum. The grand mean of 1414.11 µS/cm serves as the conductivity value carried by the produced quality control material. The close agreement between the bottle means and the grand mean further supports the uniformity of the measurement process.

3.4. Uncertainty of the Measurement Results

The uncertainty in the results of the characterized conductivity consists of two parts: the first is the uncertainty in the molality of the prepared KCl solution and the second is the uncertainty of the measured conductivity during characterization of the QCM. The estimation of uncertainty has been performed in accordance with the ISO GUM and EURACHEM/CITAC guide CG4 [18,19].

3.4.1. Uncertainty of the KCl Molality

The molality of the prepared KCl solution was calculated using the mathematical model in equation 2. From this model, the sources of uncertainty of the KCl molality can be identified as: mass of KCl (m_1), purity *(p)*, molecular weight (*MW*) and mass of solvent (m_2). The uncertainty of each of them was estimated as described below.

3.4.1.1. Purity (p)

The purity of KCl was 99.5-100.5% (i.e .100±0.5%) and its standard uncertainty was obtained using Equation 6 and was found 0.0029.

$$u_p = \frac{U_{\exp}}{\sqrt{3}} \qquad (6)$$

3.4.1.2. Mass of KCl (m_1)

The uncertainty associated with the mass of KCl, m_1 was estimated using Equation 7 where m is the mass of sample multiplied by a calibration factor quoted from the calibration certificate of the balance and was found to be ±0.00000053 g.

$$u_m = \sqrt{\left(\frac{Max\,error}{\sqrt{3}}\right)^2 + 2\left(m\,.\,Cal\ factor\right)^2} \qquad (7)$$

3.4.1.3. Molecular Weight of KCl

According to IUPAC publication concerning the standard atomic weights of elements and their associated uncertainties, the data for potassium and chlorine are presented in Table 7 [25].

Table 7. the standard atomic weights and uncertainty of K and Cl.

Element	Symbol	Atomic number	Standard atomic weight	Uncertainty
Potassium	K	19	39.0983	0.0001
Chlorine	Cl	17	35.45	0.01

From this table, the reported uncertainty was divided by √3 to obtain the standard uncertainty of the molecular weight of K and Cl. Then, the combined standard uncertainty of the molecular weight of KCl was calculated according to Equation 8 as 0.000077 where c_1 and c_2 are sensitivity coefficients and each equal 1 since uncertainty is expressed in the same unit, g/mol [19].

$$u_{MW\ KCl} = \sqrt{(c_1.u_{MW\ K})^2 + (c_2.u_{MW\ Cl})^2} \qquad (8)$$

3.4.1.4. Mass of Solvent (m_2)

The uncertainty of the mass of solvent, m_2 was calculated the same way as m_1 using equation 7 and was found to be 0.00051g.

The combined standard uncertainty u_c, of the KCl molality (m) was calculated using Equation 9 where m is the molality and was find to be 0.000029 mol/kg.

$$u_c = m\sqrt{\left(\frac{u_m}{m_{KCl}}\right)^2 + \left(\frac{u_p}{p}\right)^2 + \left(\frac{u_{MW}}{MW_{KCl}}\right)^2 + \left(\frac{u_m}{m_{Solv}}\right)^2} \qquad (9)$$

3.4.2. Uncertainty of the Conductivity of the QCM

The conductivity of the quality control material was calculated using Equation 10 in which α is the temperature coefficient and was taken as *2%/k* [26,27].

$$k_{25} = \frac{k_T}{1 + \alpha\,(T - 25\ °\mathrm{C})} \qquad (10)$$

where,

k_{25} - conductivity calculated at 25°C

k_T - conductivity measured at temperature *T °C*
α_{25} - temperature coefficient which is taken as *2%/k*

From Equation 10, explicit sources of uncertainty can be identified as: CRM, temperature effect on the CRM and the temperature effect on the measuring electrode. On the other hand, implicit sources of uncertainty can be estimated from the instrument accuracy, resolution and measurement repeatability. All sources of uncertainty related to both KCl molality and conductivity measurements are summarized in the fishbone diagram presented in Figure 2.

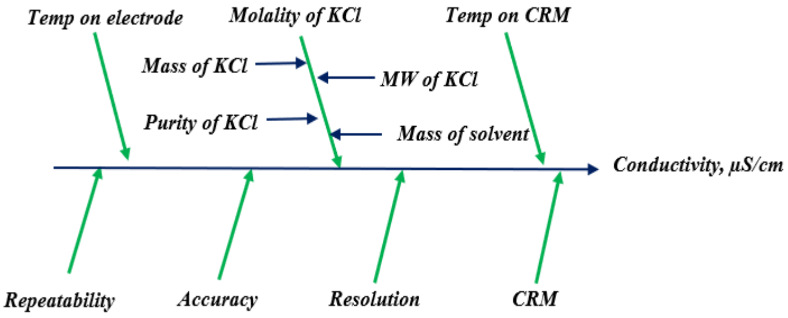

Figure 2. Fishbone structure showing all uncertainty sources

3.4.2.1. Uncertainty from Explicit Sources

3.4.2.1.1. Certified Reference Material (CRM)

The standard uncertainty of the CRM, denoted as u_{CRM} was calculated by dividing the expanded uncertainty stated in the CRM certificate by 2 using Equation 11.

$$u_{CRM} = \frac{U_{CRM}}{2} \quad (11)$$

3.4.2.1.2. Temperature Effect on the CRM

The CRM certificate provides conductivity values at both 20 °C and 25 °C. The difference in conductivity (ΔEC) and temperature (ΔT) were used to calculate the sensitivity coefficient (c_i) by the relation $c_i = \Delta EC/\Delta T$. The resulting coefficient was found 20.6 µS·cm$^{-1/°C}$. This value was then multiplied by the standard uncertainty of the calibrated thermometer, *u(t)* (±0.02 °C) to calculate the uncertainty associated with the temperature influence on the CRM using Equation 12. The resulting uncertainty was found to be ±0.21 µS/cm.

$$u_{T_{CRM}} = u_{t\ thermometer}\ x\ c_i \quad (12)$$

3.4.2.1.3. Temperature Effect on the Electrode

The conductivity, k_T at the solution temperature (24.9 °C) was calculated using Equation 13 and was found to be 1413.5 µS/cm [26].

$$k_T = k_{25}\ x\ [1 + \alpha(T - 25)] \quad (13)$$

The uncertainty associated with the electrode response to temperature was taken as the difference between the conductivities at 25 °C and 24.9 °C using Equation 14.

$$u_{T\ electrode} = k_{25} - k_T \quad (14)$$

The combined uncertainty of the two temperature related contributions was determined by Equation 15, resulting in a value of ±0.35 µS/cm. In this equation, c_1 and c_2 represent the sensitivity coefficients, calculated as 20.6 $\mu S \cdot cm^{-1/°C}$ and 1 respectively.

$$u_c\,(T) = \sqrt{\left(c_1 \,.\, u_{T\,CRM}\right)^2 + \left(c_2 \,.\, u_{T\,elect}\right)^2} \qquad (15)$$

3.4.2.2. Uncertainty from Implicit Sources

Implicit sources of uncertainty were incorporated into the model equation 10 as a single uncertainty term, Δk of zero conductivity but with an uncertainty value as shown in Equation 16 [28, 29].

$$k_{25} = \frac{k_T}{1 + \alpha\,(T - 25°C)} + \Delta k \qquad (16)$$

The term Δk was estimated from the resolution and accuracy of the conductivity-meter in addition to the repeatability of measurements as described below.

3.4.2.2.1. Resolution Uncertainty

To calculate the standard uncertainty (u_{Resol}), the resolution was divided by 2√3, assuming a rectangular distribution using Equation 17 to give an uncertainty of 0.29 µS/cm.

$$u_{Resol} = \frac{Resolution}{2\sqrt{3}} \qquad (17)$$

3.4.2.2.2. Accuracy Uncertainty

The specified accuracy (%) in the instrument manual was divided by √3 to yield the standard uncertainty (u_{Accu}) as in Equation 18. The resulting value was then multiplied by the measured conductivity to give an uncertainty of 4.081 µS/cm.

$$u_{Accuracy} = \frac{\%\ Accuracy}{\sqrt{3}} \qquad (18)$$

3.4.2.2.3. Repeatability Uncertainty

The repeatability uncertainty (u_{Rept}) was calculated using the standard deviation of the mean value divided by the square root of the number of measurements (n) in accordance with Equation 19 and was found to be 0.37 µS/cm.

$$u_{Rept} = \frac{SD}{\sqrt{n}} \qquad (19)$$

The combined standard uncertainty for the implicit sources: accuracy, resolution and repeatability was calculated using Equation 20 as 4.11 µS/cm. The sensitivity coefficients c_1, c_2 and c_3 were all set to 1 since the three uncertainties are expressed in the same unit, µS/cm.

$$u_{\Delta k} = \sqrt{\left(c_1 \,.\, u_{Resol}\right)^2 + \left(c_2 \,.\, u_{Accur}\right)^2 + \left(c_3 \,.\, u_{Rept}\right)^2} \qquad (20)$$

3.4.2.3. The Combined Standard Uncertainty

To calculate the combined standard uncertainty, Equation 16 was differentiated to obtain the relevant sensitivity coefficients shown in Formulas, 21-23.

$$\frac{\delta k_{25}}{\delta k_T} = \frac{1}{\alpha\,(T - 25°C) + 1} \tag{21}$$

$$\frac{\delta k_{25}}{\delta T} = \frac{k_T \alpha}{[\alpha\,(T - 25) + 1]^2} \tag{22}$$

$$\frac{\delta k_{25}}{\delta \Delta k} = 1 \tag{23}$$

These coefficients were then used to calculate the combined standard uncertainty, u_c by Equation 24. The final value was found to be 11.55 µS/cm and is presented in Table 8.

$$u_c = \sqrt{\left(\frac{\delta k_{25}}{\delta k_T} \cdot u_{CRM}\right)^2 + \left(\frac{\delta k_{25}}{\delta T} \cdot u_T\right)^2 + \left(\frac{\delta k_{25}}{\delta \Delta k} \cdot u_{\Delta k}\right)^2} \tag{24}$$

Table 8. The uncertainty budget of the conductivity (1414.11 µS/cm) of the quality control material

Uncertainty part	Source		Estimate	*u(x_i)*	Unit	Distribution	*c_i*	*c_i. u(x_i)*
KCl molality	Mass of KCl		5.60775	0.00000053	g	Normal	1	0.00000053
	Purity		0	0.0029	%	Rectangular	1	0.0029
	MW of KCl		0	0.0058	g	Rectangular	1	0.0058
	Mass of solvent		0	0.00051	g	Normal	1	0.00051
Conductivity measurements	CRM		1410.6	1.4	µS/cm	Normal	1	1.4
	Temp on CRM		0	0.21	µS/cm	Rectangular	20.6	0.35
	Temp on electrode		0	0.28	µS/cm	Rectangular	1	
	Δk	Resolution	0	0.29	µS/cm	Rectangular	1	4.10
		Accuracy	0	4.082	µS/cm	Rectangular		
		Repeatability	0	0.17	µS/cm	Normal		
Combined standard uncertainty, u_c			11.55					
Expanded uncertainty, U_{exp}			23.10 µS/cm or 1.63%					

After evaluation of the standard uncertainty for the molality of the KCl solution and the conductivity of the quality control material, the combined standard uncertainty (u_c) was calculated using Equation 25. The obtained u_c value of 11.55 was then multiplied by a coverage factor (*k=2*) yielding an expanded uncertainty of 23.10 µS/cm or 1.63%.

$$u_c = k\sqrt{\left(\frac{u(k)}{k}\right)^2 + \left(\frac{u\,(M)}{M}\right)^2} \tag{25}$$

3.5. The Stability of the QCMs

The short-term stability study was performed over a four weeks period to verify the stability of the QRM under transport conditions. The measurements were performed using a calibrated conductivity meter and the results obtained were recorded in Table 9.

Table 9. the conductivity results of the QCM stored samples at different temperatures

Storage time (W)		Conductivity, µS/cm	Normalized conductivity values
4 weeks storage at Room temperature (21 °C)		1414.33	1
4 weeks storage at 4 °C	W 1	1415.00	1.0005
	W 2	1413.00	0.9991
	W 3	1414.00	0.9998
	W 4	1414.33	1.0000
4 weeks storage at 40 °C	W 1	1415.67	1.0009
	W 2	1411.67	0.9981

W 3	1413.00	0.9991
W 4	1415.00	1.0005

In order to assess the short-term stability, a normalization approach was applied to the measured conductivity values. The value measured at room temperature was used as a baseline and was divided by itself to be normalized to 1. Then all the measured values obtained after various storage durations were divided by this baseline value and the normalized data were presented in Table 7. To investigate the potential time dependent variability, the normalized conductivity values were plotted against storage duration as shown in Figure 3.

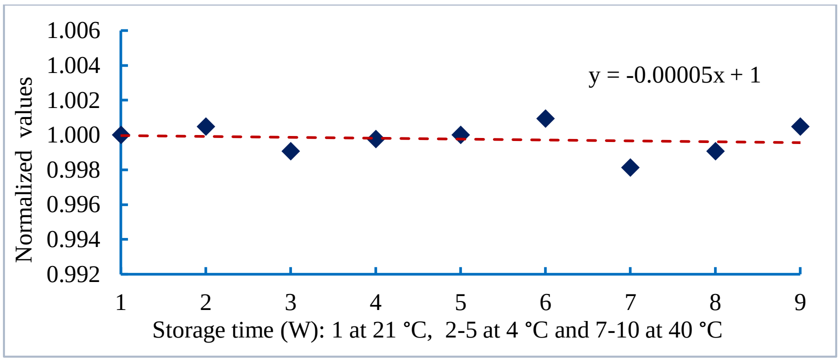

Figure 3. The regression line of the normalized conductivity values under different storage conditions

The dispersion of data points around the regression line suggests no systematic deviation indicating that the conductivity of the samples remained stable over the course of the thermal storage conditions. To evaluate whether any trend was present in the data, a linear regression analysis was performed. The critical question was whether the slope of the regression line significantly deviates from zero, which would indicate a time dependent change. The results of the regression analysis are summarized in Table 10, including the estimated slope (b_1), its standard error $s(b_1)$ and the corresponding p-value. A t-test was carried out to test the null hypothesis, H_0 that the slope is zero, using the statistic $t=|b_1/s(b_1)|$[28,29].

Table 10. The regression parameters of short-term stability data of the QCM

	Coefficients	***Standard Error***	***t-Stat***	***P-value***
Intercept	1.000019509	0.000676	1479.748789	1.70002E-20
X Variable 1	-0.000051	0.000120	-0.42455221	0.68

The calculated t-value was found to be 0.425, which is markedly lower than the $t_{critical}$ of 2.365 at a 95% confidence level with df =7. This confirms that the slope is not statistically different from zero and therefore no significant trend is present. Furthermore, the p-value of 0.68 exceeds the conventional threshold of 0.05 supporting the conclusion that the data do not exhibit any instability or drift over the shipment period. On the other hand, the long-term stability of the QCM was taken as two years as specified in the certificate of the CRM used for calibration of the conductivity meter.

3.6. The Traceability of the Conductivity Measurement Results

The traceability of primary level conductivity measurements is directly ensured by their linkage to the SI units of meter (m), kelvin (K), and ohm (Ω). The establishment of the traceability chain for electrolytic conductivity measurements was reported [30]. At the top of this chain, the Jones cell was employed as the primary standard with a measurement uncertainty of U_{exp} = 0.2 µS/cm, providing the direct realization of electrolytic conductivity in terms of SI units. In the present work, we have established the traceability of the conductivity measurement results to the SI units through the use of a certified reference material (CRM) produced by an NMI signatory to the CIPM MRA.

3.7. Application of the QCM in Developing a Quality Control Chart

The performance of the prepared quality control material (QCM) was assessed by constructing a control chart and monitoring its stability over a six weeks period. A single bottle of the QCM batch was selected and 6 conductivity measurements were carried out at 25 °C each week. This process yielded six subgroups of results as presented in Table 11.

Table 11. the conductivity results (µS/cm) in 6 weeks for the quality control chart

W1	**W2**	**W3**	**W4**	**W5**	**W6**	$\bar{x}$	**Grand Mean**	***R***	$\bar{R}$
1415	1415	1414	1415	1415	1415	1414.17	1414.61	1	1.17
1414	1415	1414	1415	1415	1415	1414.83		1	
1413	1415	1414	1415	1415	1415	1414.33		2	
1414	1415	1415	1415	1414	1415	1414.83		1	
1415	1414	1414	1415	1415	1414	1414.83		1	
1414	1415	1415	1414	1415	1414	1414.67		1	

The grand mean of the conductivity measurements was found to be 1414.61 µS/cm and was designated as the control value. For each subgroup, the range, *R* (the difference between the maximum and minimum values) was determined and the average, $\bar{R}$ was calculated as 1.17. Based on Equations 26 and 27, the lower control limit (LCL) and upper control limit (UCL) were calculated as 1414.05 and 1415.17 respectively [31].

$$LCL = \bar{x} - A_2 \, . \, \bar{R} \quad (26) \qquad\qquad UCL = \bar{x} + A_2 \, . \, \bar{R} \quad (27)$$

The constant A_2 corresponding to a sample size of $n = 6$ was obtained from a standard statistical table and found to be 0.48. The control chart, illustrated in Figure 4 contains a solid line representing the control value and dashed lines indicating the UCL and LCL. The weekly mean values of the six measurements were plotted as solid dots.

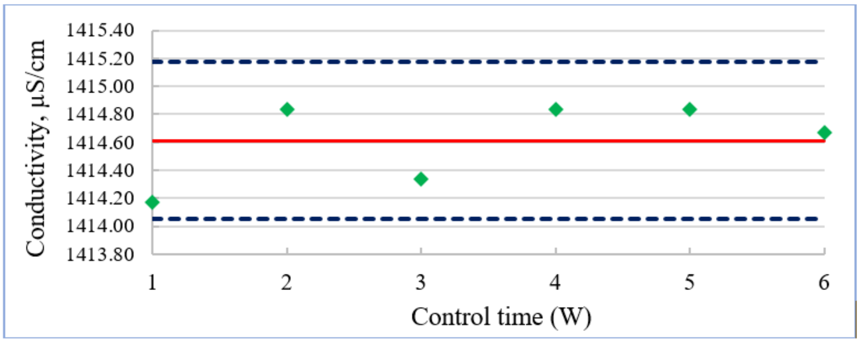

Figure 4. The quality control chart for conductivity measurements using the prepared QCM.

It can be seen from the figure that, all data points are randomly distributed around the control value and remained within the control limits. These results clearly demonstrate the stability and repeatability of the measured values, confirming that the prepared QCM is suitable for its intended application in quality control of conductivity measurements. The QCM can also be used as proficiency testing samples to help accredited laboratories improve their performance. Uysal et al reported the organization of a proficiency tesing (PT) in conductivity testing in water and soil applications in accordance with the requirements of ISO 17043 [32]. They prepared the conductivity PT samples and analyzed the results of 77 participants who carried out their measurements using conductivity meters. The results proved that the PT programme offered the participants a very good opportunity to strengthen both the accuracy and the reliability of their measurement results.

4. Conclusions

A batch of a quality control material from KCl solution was prepared with a target conductivity value of 1414 µS/cm based on ISO/TR 33402 requirements. The solution was dispensed into 30 HDPE bottles each is 250 mL. Homogeneity was evaluated by measuring the conductivity of systematically selected 10% of the units. ANOVA results confirmed the homogeneity of the batch as the F_{calc} (0.714) was lower than the F_{critc} (3.682) and the p-value exceeded 0.05. The regression analysis of the short-term stability under different thermal storage conditions showed no significant trend, where the t-statistic (0.425) was less than the $t_{0.05,n-2}$ (2.365). Characterization measurements conducted over three different days yielded an average conductivity value of 1414.11 µS/cm with an expanded uncertainty of 1.63% demonstrating the material stability and suitability for quality control purposes. The quality control chart developed using the prepared material for 6 weeks showed the QCM is suitable to the purpose. These findings confirm that the prepared KCl solution is appropriate for use as a QCM in the routine conductivity measurements in food and environmental fields and as a PT sample to demonstrate competency of accredited laboratories.

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