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GENERAL PAPER

Short- and long-term stability of electrolytic conductivity certified reference materials

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Abstract

Electrolytic conductivity is a common parameter measured within industry. Proper usage of electrolytic conductivity sensors requires the periodic calibration using solutions of known conductivity. This parameter can be disseminated through the use of certified reference materials (CRMs) produced according to ISO 17034. A part of the certification of reference materials relates to their stability both in the material they are packaged in and as a function of time, both at the short- and long-time scales. Electrolytic conductivity CRMs produced at DFM A/S are evaluated for the stability in various bottle types, and under various storage and transport conditions. Materials with nominal conductivity values between 10 mS m^{-1} and 10 mS m^{-1} are shown to be stable at short-time (~ 1 month) and long-time (expected shelf life and beyond) scales.

Keywords Electrolytic conductivity · Stability · Storage · Transportation · CRM

Introduction

Electrolytic conductivity is a readily assessable measure of the total content of charge-carrying species in solution, commonly aqueous solutions [1]. For routine analysis, electrolytic conductivity is measured using conductivity sensors, which require calibration. To ensure metrological traceability, and thus to ensure comparability between results [2], calibration can be performed using certified reference materials (CRMs) in the appropriate conductivity range. CRMs produced by National Metrology Institutes (NMIs) [3] have several features which may be desirable, depending on the application, including: measurement methods with established traceability to the International System of Units (SI), often via a primary method [4]; small assigned uncertainties [5]; and regular participation in multilateral comparisons, demonstrating both measurement (e.g., CCQM-K36.2016) and CRM production capabilities (e.g., CCQM-P143) organized through the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) [6].

ISO 17034:2016 [7] specifies the requirements for the production of CRMs. Several key steps are outlined, including (non-exhaustively) the following:

- Assessment of homogeneity (7.10), including homogeneity in the final packaging, and assessment of its contribution to the uncertainty
- Monitoring of stability (7.11), and its contribution to uncertainty, under (i) long-term storage and (ii) transport conditions
- Assignment of property values (7.13), including identification of contributions to uncertainty

Technical recommendations regarding the assessment of homogeneity and stability are provided in ISO Guide 35:2017 [8]. Regarding stability assessment and monitoring (section 8), several assessment methods are proposed, including classical and isochronous studies. Classical stability studies (and monitoring) include intermediate conditions of measurement, whereby measurements are taken at prescribed intervals (e.g., every 3 months), and real-time stability studies, whereby a measurement is taken at frequent intervals (e.g., every 2 weeks) over the CRMs lifetime. The former is often performed on CRM batches available for use (i.e., sold commercially) in order to verify continued stability, while the latter is performed during the testing phase, whereby a complete batch of reference material is consumed

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to more fully investigate long-term stability. Accelerated stability studies (8.3.3.2), which can emulate both long-term storage and transport conditions, typically include exposure of CRMs to more extreme conditions (e.g., higher and lower temperatures, sources of light, humidity, etc.) than recommended for either storage or transport.

DFM, the Danish National Metrology Institute, produces electrolytic conductivity CRMs at four conductivity levels: 10 mS m^{-1}, 100 mS m^{-1}, 1 S m^{-1}, and 10 S m^{-1}. Reference material for certification is produced in large batches, followed by distribution into final packaging (bottling). Depending on the batch size, a representative number of bottles are selected for assignment of the property value. Electrolytic conductivity is assessed using secondary Jones-type electrolytic conductivity cells [9, 10], which have their cell constants regularly calibrated against a primary cell [4]. CRM electrolytic conductivity values and associated uncertainties are assigned based on repeat measurement values (i.e., $n > 1$, where n is the number of measurements), between-bottle dispersion (i.e., homogeneity studies), and maximum allowed drift over the lifetime of the material (i.e., pre-set long-term stability limits). Long-term stability is monitored under intermediate conditions of measurement, with electrolytic conductivity measured on randomly selected bottles at 3-month or 6-month intervals, depending on the lifetime of the CRM (conductivity level dependent).

Prior reports on CRM long-term stability available in the literature have focused primarily on the influences of various forms of packaging (e.g., bottle types) and storage conditions over periods of several months to several years, depending on conductivity level. Investigated packaging options have included various glass containers [11] and plastic bottles [1, 12]. The appropriate storage vessel type and material (including type of glass and plastic (e.g., high-density polyethylene (HDPE) versus polyethylene terephthalate (PET) [12]) were found to be conductivity level dependent.

Reported storage conditions have focused on storage temperature, including ambient (20 °C – 25 °C) and refrigerated (4 °C) conditions [12–14]. Interestingly, Barron and Ashton reported a 0.5 mS m^{-1} CRM (reported as 5 µS cm^{-1}), stored in HDPE bottles that became unstable after only 2 weeks of storage at 4 °C [12], while Fraga et al. reported stability for 56 weeks for a 0.15 mS m^{-1} CRM, stored in borosilicate glass bottles, under identical, refrigerated conditions [13].

In the literature, reports dealing with the short-term stability, emulating transport conditions, are relatively rare. Shreiner [11] remarked that screw-top bottles had been observed to leak, on occasion, during CRM transport, while Fraga et al. [13] stored a 0.15 mS m^{-1} CRM at 50 °C for 7 days to 21 days, emulating the potential effects of transport under uncontrolled temperature conditions. No change in electrolytic conductivity value was observed, implying stability under prolonged transportation conditions.

Here, additional stability studies including investigations of the influence of packaging, transport, and short-term storage conditions are reported, as well as real-time stability studies for the specified lifetime, and beyond, of electrolytic conductivity CRMs routinely produced at DFM (10 mS m^{-1}, 100 mS m^{-1}, 1 S m^{-1}, and 10 S m^{-1}) are reported. Results confirm the long-term stability of CRMs under suggested storage conditions (real-time stability studies), the suitability of packaging during international shipping (transportation stability) and show CRM stability over a wide range of short-term storage conditions (storage temperature and exposure to light).

Experimental methods

Electrolytic conductivity solutions (nominal values: 10 mS m^{-1}, 100 mS m^{-1}, 1 S m^{-1}, and 10 S m^{-1}) were produced using KCl (> 99.9 % purity, VWR) and ultra-pure water (UPW) (Milli-Q, Millipore, Merck, > 18 MΩ cm), in 11-kg or 22-kg batches, according to internal DFM procedures. An appropriate mass of UPW was rapidly stirred overnight in order to saturate the water relative to atmospheric CO_2 levels. An appropriate (excess) amount of KCl was dried at 500 °C for 4 h, cooled to between 100 ºC and 200 °C in the oven, before being moved to a desiccator, and allowed to cool to room temperature. CO_2-saturated UPW and dried KCl were carefully weight out and combined. Ambient temperature, relative humidity, and pressure conditions were recorded.

The produced solutions were allowed to stir, sealed, for at least 2 h. A sample (~ 300 mL) of each was taken, and the electrolytic conductivity was evaluated at 25 °C using a secondary Jones-types cell of the appropriate cell constant. When the determined conductivity value deviated from established tolerances for each conductivity level, the solutions were adjusted through the addition of KCl or UPW, as appropriate. The adjusted solutions were stirred for at least another 2 h before another sample was taken to verify conductivity is within tolerances at 25 °C.

The solutions were stirred, sealed, overnight. Bottling was performed the morning, following manufacture of the solution and acceptance of the samples. Each batch of solution was transferred into bottles, typically 500-mL DURAN glass bottle: 21 bottles and 42 bottles, for 11-kg and 22-kg batches, respectively. These bottles possess a ‘fill line’ roughly indicating the 500-mL fill-point. Bottles were filled to the fill line, leaving several centimeters of headspace between the liquid level and cap. Glass bottles were tightly caped and well wrapped in Parafilm. A representative number of bottles from each batch were set aside for simultaneous property value determination and homogeneity testing: 3 bottles and 5 bottles, for 11-kg and 22-kg batches, respectively. Each batch was assigned a reference electrolytic conductivity value within 1 week of production.

Characterization of electrolytic conductivity

For each electrolytic conductivity solution, a secondary Jones-types conductivity cell with an appropriate cell constant was employed during characterization. Measurement of electrolytic conductivity at DFM, and its traceability to the SI, has been well described elsewhere [10, 15]. Briefly, several fixed-geometry Jones-types cells of varying cell constants, consisting of two Pt-electrode disks embedded in a fixed glass body, are routinely calibrated using a reference solution against a variable-geometry, primary electrolytic conductivity cell, equipped with two center pieces of known dimensions [4]. Metrological traceability is realized through calibration of secondary cells against the primary cell of known length (cell constant calibration, traceable to the meter), use of calibrated resistors during impedance measurements of solution resistance, and use of calibrated thermometers.

Electrolytic conductivity solutions are poured into the fixed-geometry Jones-type cell and, following equilibration, are placed in a thermostated bath, with a stability of 5 mK. Temperature is measured using a calibrated PT100 thermal probe. The temperature set point is cycled between 24 °C, 25 °C, and 26 °C, with at least 30 replicate measurements made at 25 °C. Data taken 24 °C and 26 °C are employed to determine the temperature coefficients of the solution. Resistance measurements, by electrochemical impedance spectroscopy (EIS), are made using a meter capable of measuring inductance (L), capacitance (C), and resistance (R) (Agilent/Keysight E4980 LCR Meter), with its function verified before use against a calibrated resistor. EIS is acquired within the range 300 Hz and 9000 Hz, the exact frequency range being solution resistance dependent, with the characteristic resistance value extracted by extrapolating the real part of resistance against inverse frequency ($1/f$) to zero.

Environmental conditions, including atmospheric pressure and CO_2 volume fraction (measured as parts per million as volume fraction (ppm) CO_2 in air), are monitored, as the influence of dissolved CO_2 on aqueous electrolytic conductivity solutions is applied [15]. Due to exchange with the laboratory air in the handling of cells and solutions, it is assumed that an equilibrium is achieved between the atmospheric carbon dioxide content and the solution. However, to take into account potential shifts in this equilibrium, a contribution to the uncertainty of the measured conductivity from the dissociation of carbon dioxide in water given by the sensitivity coefficient at 380 ppm CO_2 was found in the literature [16] (with uncertainty estimated from trust in source) as (0.11 ± 0.05) μS m^{-1} ppm^{-1}. The carbon dioxide volume fraction and atmospheric pressure of the CRM manufacturing and electrolytic conductivity measurement laboratories were continuously monitored using traceable instruments. If these did not deviate from pre-set tolerances ((450 ppm ± 75 ppm) at 23.0 °C ± 0.5 °C and 45 % ± 5 % relative humidity), this standardized uncertainty component for the influence of atmospheric carbon dioxide volume fraction was applied to the electrolytic conductivity of aqueous solutions.

The standard uncertainty of measurement ($u_{\text{measurement}}$) of each batch, or individual bottle, of solution was evaluated using a full uncertainty budget, performed using an in-house program (DFM-GUM ver. 2.1b) based on the ISO Guides to the expression of uncertainty in measurement (GUM). Each electrolytic conductivity solution batch was assigned a batch reference value, and an uncertainty taking into account characterization, homogeneity, and long-term stability assigned from prior tests. Contributions to standard uncertainty are summarized graphically in Fig. 1, including the uncertainty due to characterization ($u_{\text{measurement}}$), and that of the reference material (RM), denoted u_{RM}. A more detailed breakdown of the general contributions to uncertainty electrolytic conductivity is available elsewhere [5], as well as a DFM-specific breakdown [10]. More details related to contributions to uncertainty due to LCR calibration (including the use of reference resistors) cell constant calibration, etc., may be found in [15].

Bottle type

Several 11-kg batches of solutions with nominal conductivities of 100 mS m^{-1} were produced. Individual batches were bottled into various bottle types, including: 500 -mL LDPE bottles, 250-mL glass bottles with vial-type caps, 250-mL and 500-mL DURAN glass bottles. Bottles, selected at random, were regularly tested over the following 52 weeks. Bottles were stored away from daylight at 23.0 °C ± 0.5 °C and 45 % ± 5 % relative humidity.

Bottles were purchased from commercial suppliers. Upon receipt, glass bottles were thoroughly rinsed using deionized (DI) water (~ 1.3 mS m^{-1} at 23 °C). Bottles were filled, without headspace, with DI water and capped. Filled bottles stood overnight before being emptied and dried at 120 °C for 6 h to 8 h. Washed bottles were allowed to cool in the drying oven (overnight), before being capped and stored in their shipping boxes until use.

Long-term stability

Batches of 10 mS m^{-1}, 100 mS m^{-1}, 1 S m^{-1}, and 10 S m^{-1} solutions, in 500-mL DURAN glass bottles, were stored away from daylight at 23.0 °C ± 0.5 °C and 45 % ± 5 % relative humidity. Bottles were selected randomly throughout the shelf life of each reference material and beyond

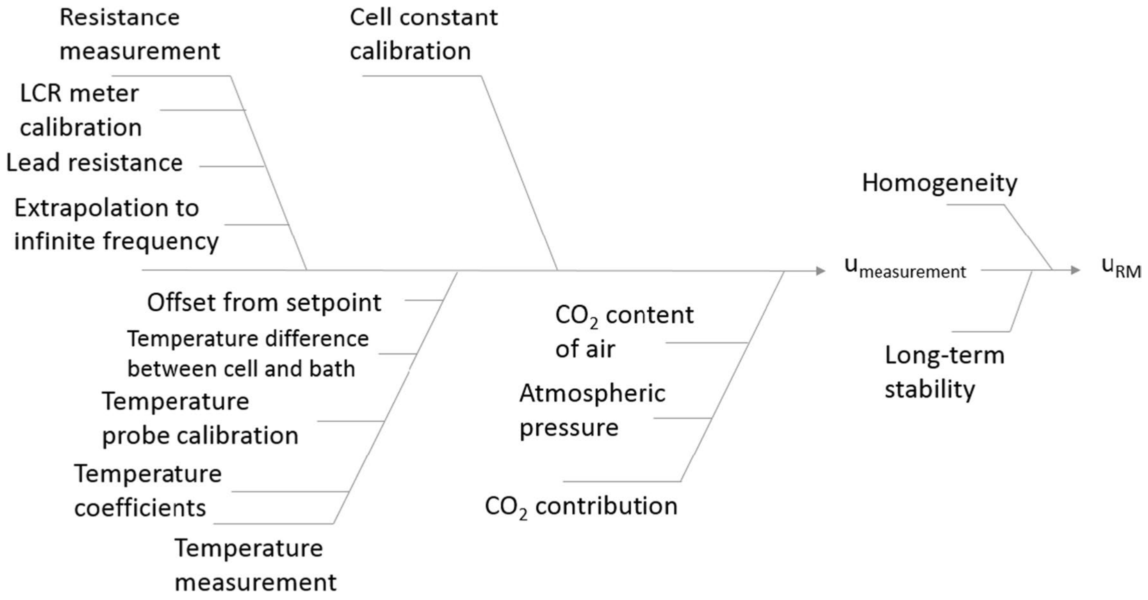

Fig. 1 Contributions to uncertainty of electrolytic conductivity characterization ($u_{\mathrm{measurement}}$) and associated with a reference material (u_{RM}) with this property value

(10 mS m^{-1}, 6-month lifetime + 6 months; 1 S m^{-1}, 1-year lifetime + 6 months), for regular electrolytic conductivity testing.

Short-term stability and transport conditions

A 22-kg batch with a nominal conductivity value of 10 mS m^{-1} was produced and bottled into 21 DURAN glass bottles, and 21 Kimble glass bottles, both 500 mL. Both glass bottle types were specified by their distributors as having a similar high-quality borosilicate composition. The electrolytic conductivity reference value and homogeneity of the batch were determined using three bottles of each type. Pairs of bottles (at least one DURAN and one Kimble) were treated identically under one of the following conditions:

- Bottles were packaged and shipped, by air transport, two times 7200 km (shipped and returned). The duration of each shipping was 3 days. Shipment took place during the month of July, without provisions for temperature control.
- Storage for 3 days with direct exposure to sunlight (well-illuminated, south-facing window), then in a refrigerator at 5 °C, and finally in an oven at 30 °C and 40 °C.
- Storage for 3 days at 5 °C, followed by 1 month with direct exposure to sunlight
- Air transport (as described above), followed by 1 month at 5 °C
- Storage for 3 days at 30 °C and then a further 1 month at 30 °C

From the original 22-kg batch, pairs of bottles (DURAN and Kimble glass) were set aside for a monitoring study, with electrolytic conductivity re-evaluated on at least two bottles (one of each glass composition) every 3 months. CRM bottles were stored, sealed in Parafilm, under recommended storage conditions (room temperature, away from direct sunlight). Re-evaluations were performed after 3 months and 6 months, during the shelf life of the CRM (6 months), as well as beyond (9 months and 12 months from production date). Additionally, a pair of bottles were stored for 4 months with Parafilm sealing under recommended storage conditions. At this point, the Parafilm was removed, and bottles were stored, under identical conditions, for a further 3 months.

The influence of transport, short- and long-term storage, as well as potential influence of bottle types, on electrolytic conductivity was evaluated.

Results and discussion

Bottle type

Four batches of 100 mS m^{-1} reference material (RM) were produced, and each was bottled in bottles of varying volume and composition, as detailed in Table 1. Following assignment of reference electrolytic conductivity values (Table 1), randomly selected bottles from each batch were tested regularly over the shelf life of this RM, 52 weeks. For each bottle type, electrolytic conductivity is shown as a function of time in Fig. 2.

Table 1 Bottle material and reference electrolytic conductivity value assigned to the batches of 100 mS m^{-1} reference material

Bottle type	Bottle volume (mL)	Reference value (mS m^{-1}), 25 °C ± expanded uncertainty (k = 2)
Glass, vial caps	250	100.11 ± 0.14
LDPE	500	100.13 ± 0.14
DURAN glass	250	100.09 ± 0.14
DURAN glass	500	100.00 ± 0.16[a]

[a]CM1418, 100 mS m^{-1}, stability measured as part of CCQM-P143 (unpublished data)

Figure 2 includes horizontal dashed lines which show standard (u_{RM}) and expanded uncertainty (U_{RM}, $k=2$) assigned to each RM batch, including contributions of homogeneity and stability. Additionally, dashed lines forming a cone express the progress of the internal tolerance interval (TI) over the shelf life of the RM—this value expresses the allowed limits set for the change in electrolytic conductivity as a function of time, i.e., following reference value ($\mathrm{CRM}_{\mathrm{value}}$) assignment (time ≤ 1 week), measured electrolytic conductivity values should fall inside this cone at any given time. This internal TI is calculated based on the uncertainty associated with (a) 'dispersion of a single sample,' associated with the variability of a single sample and the average of n samples (homogeneity), and (b) the assigned drift tolerance over the shelf life of an individual CRM conductivity level.

$$\mathrm{TI} = \mathrm{CRM}_{\mathrm{value}}\left[1 \pm \sqrt{\left(a^2 + b^2\right) * 2}\right]$$

The 'dispersion of a single sample' is calculated from the 'single sample factor' (f) and the maximum relative standard deviation taken from the replicate (n) measurements made to assign the $\mathrm{CRM}_{\mathrm{value}}$ ($n = 3$ to 5).

$$f = \sqrt{\frac{n-1}{n-3}\left(1 + \frac{1}{n}\right)},\ n > 3$$

$$f = \frac{u_{95}\sqrt{1 + \frac{1}{n}}}{2},\ n \leq 3$$

where u_{95} is the Student's t test distribution at 95 % confidence interval for n-1 degrees of freedom [17].

Figure 2a shows that 250-mL glass bottles with vial caps are an unsuitable bottling option for 100 mS m^{-1} reference materials. Measured values show rapid increase, exceeding expanded uncertainty within 10 weeks of storage. Measurements were discontinued due to lack of stability. Prior research on 100 mS m^{-1} reference materials (reported as 1000 µS cm^{-1}) revealed some degree of instability in serum bottles (similar to glass bottles with vial caps), but over a longer period of time (~ 1% change in conductivity over 12 months) [11]. The reference material stored in 500-mL LDPE bottle (Fig. 2(b)) showed a systematic drift in electrolytic conductivity values, with values exceeding both the internal TI cone, and the standard uncertainty, within 40 weeks following production. For both glass bottles with vial caps and LDPE bottles, conductivity increased (Fig. 2a, b), suggesting a loss of water from the reference material, possibly as a result of inferior sealing.

Two bottle types, of identical composition (DURAN glass), but differing volume (250 mL vs. 500 mL) were tested for long-term stability of a 100 mS m^{-1} reference material. As shown in Fig. 2c, the 250-mL DURAN glass bottles showed a systematic positive drift as a function of time. This trend is seen over the majority of the reference material's shelf life, with the exception of the two bottles measured at 52 weeks. These points are suspected to be anomalous, as they are strong exceptions to the trends seen over the previous ~ 40 weeks. These measurements may have been affected by non-standard laboratory conditions, including variations in temperature, atmospheric pressure, CO_2 concentration, or humidity. Despite measurements being made in a thermostated bath, variability in laboratory conditions has previously been observed to influence electrolytic conductivity results. In contrast, molality-based electrolytic conductivity CRMs (e.g., 0.01 mol kg^{-1} KCl and 1 mol kg^{-1} KCl) have been reported to show insignificant drift when stored in 250-mL DURAN glass bottles at up to 900 days [14]. However, as seen in Fig. 3b, the 500-mL DURAN glass bottles showed no systematic drift with time. As such, while the electrolytic conductivity measurements of the batch in 250-mL DURAN glass do remain within the expanded uncertainty of the reference value, bottling in the larger volume glass bottles (500 mL) shows greater stability. The cause(s) for this difference in stability due to bottle volume (250 mL vs. 500 mL) are unclear. However, both bottle volumes have the same dimension of opening (bottle neck), but the ratio of opening size to solution volume is large in the 250-mL bottles, which might cause greater drift in electrolytic conductivity value with time (poorer stability).

Long-term stability

The long-term stability of electrolytic conductivity solutions, stored in 500-mL DURAN glass bottles, sealed in Parafilm, and stored under recommended storage conditions, was evaluated. The nominal and reference electrolytic conductivity values assigned to each batch of RM and the recommended shelf life are given in Table 2. Measured electrolytic conductivity values, as a function of time, are shown in Fig. 3.

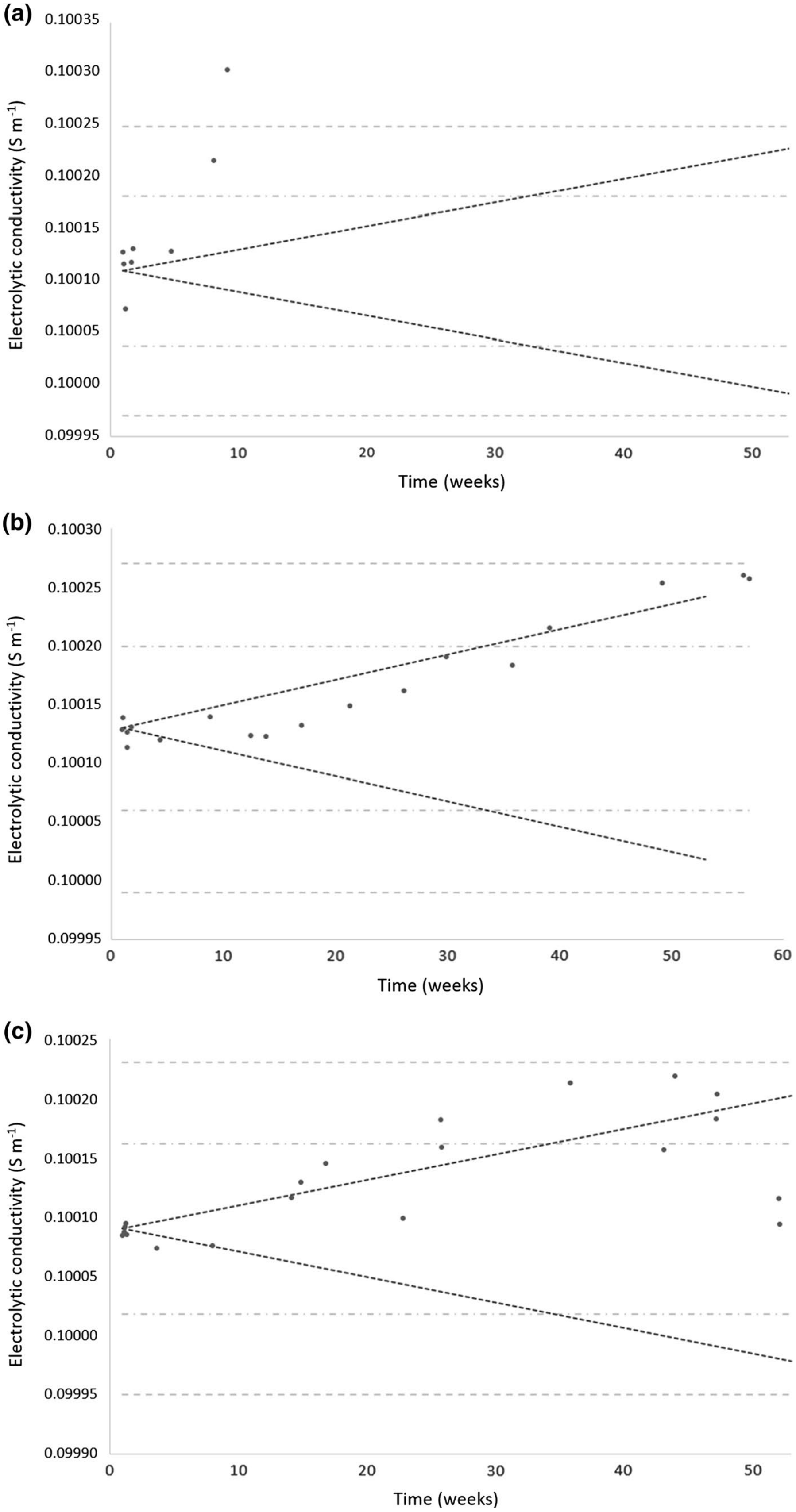

Fig. 2 Electrolytic conductivity (●) as a function of time (in weeks) for 100 mS m^{-1} RM bottled in **a** glass bottles with vial-type lids (250 mL), **b** LDPE bottles (500 mL), and **c** DURAN glass bottles (250 mL). Standard uncertainty (—•—), expanded uncertainty ($k=2$, – – –), and expected progression of internal tolerance interval (···)

Fig. 3 Electrolytic conductivity (●) as a function of time (in weeks) for reference solutions of **a** 10 mS m^{-1}, **b** 100 mS m^{-1}, **c** 1 S m^{-1}, and **d** 10 S m^{-1}. Standard uncertainty (— • —), expanded uncertainty ($k=2$, – – –), and expected progression of the internal tolerance interval (⋯)

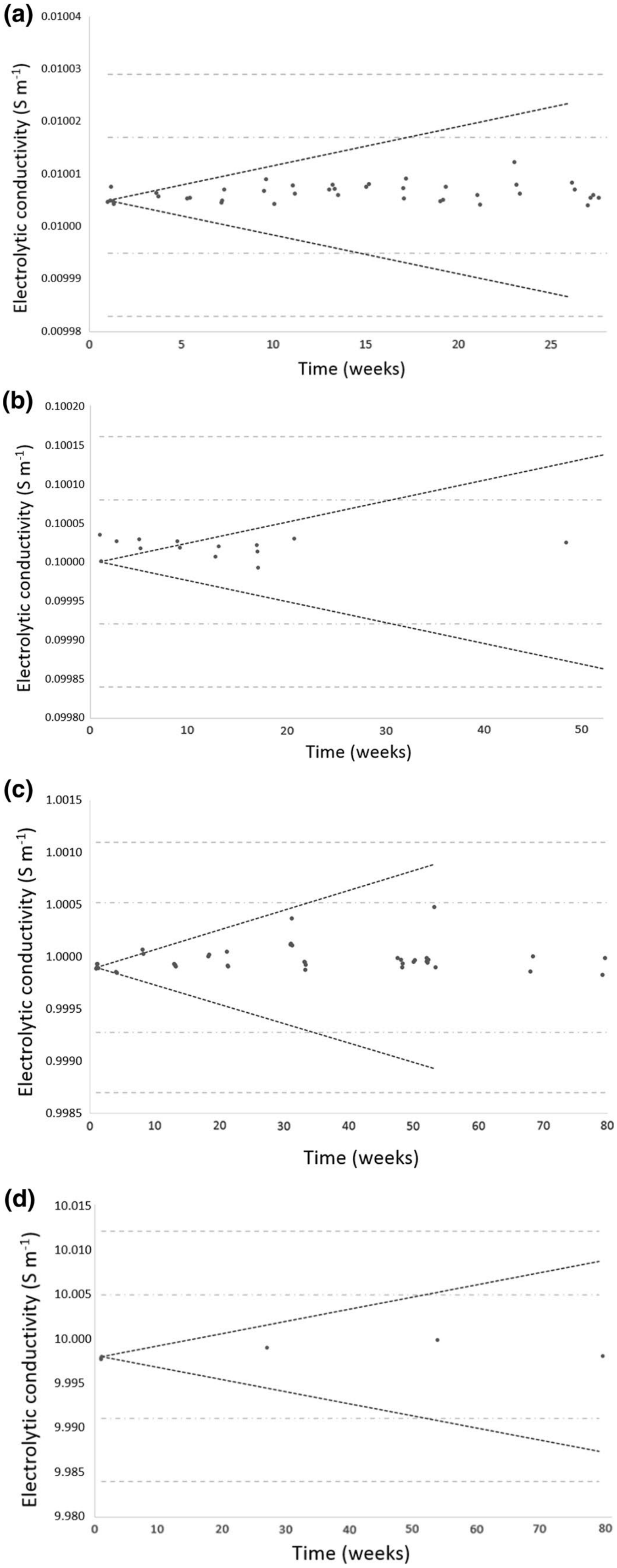

Table 2 Electrolytic conductivity solution batches—summary of nominal conductivity level, batch size, assigned conductivity value at 25 °C and expanded uncertainty over each material's shelf life (including uncertainty contributions associated with repeat measurements, homogeneity, and long-term stability)

Nominal conductivity	Batch size (kg)	Reference value (S m^{-1}), 25 °C ± expanded uncertainty (k = 2)	Shelf life (weeks)
10 mS m^{-1}	22	0.010 005 ± 0.000 025	26
100 mS m^{-1}	11	0.100 00 ± 0.000 16[a]	52
1 S m^{-1}	22	0.999 9 ± 0.001 2	52
10 S m^{-1}	11	9.998 ± 0.014	78

[a] CM1418, 100 mS m^{-1}, stability measured as part of CCQM-P143 (unpublished data)

Table 3 Electrolytic conductivities, at 25 °C, measured on 6 bottles of a 22 kg batch of 10 mS m^{-1} reference material: 3 bottles of DURAN glass, and 3 bottles of Kimble glass. Standard uncertainty is 0.005 5 mS m^{-1}, unless stated otherwise

Electrolytic conductivity (mS m^{-1})	
DURAN glass	Kimble glass
9.974	9.973
9.972	9.971[a]
9.971	9.972

[a] Standard uncertainty of 0.005 6 mS m^{-1}

A new reference material batch size was manufactured, increasing from 11 kg to 22 kg, for 10 mS m^{-1} and 1 S m^{-1} solutions. After reference value assignment and homogeneity testing within 1 week of batch production, bottles from each batch were chosen at random and tested for long-term stability approximately every 2 weeks. The 10 mS m^{-1} batch was tested over its shelf life (6 months) (Fig. 3a), showing no significant trend in electrolytic conductivity with time (slope: 4×10^{-8} S m^{-1} week^{-1}). For the 1 S m^{-1} batch, in addition to stability testing over its recommended shelf life (1 year) (Fig. 3c), bottles were selected for testing over a further 6 months. No significant trend in electrolytic conductivity was seen with time over the full 1.5 years (slope: 6×10^{-7} S m^{-1} week^{-1}), suggesting that 1 S m^{-1} reference material shelf life could be increased beyond 1 year.

Manufactured in 11-kg batches, 100 mS m^{-1} and 10 S m^{-1} reference materials' long-term stability was monitored over their shelf lives: 1 year and 1.5 years, respectively. The electrolytic conductivity of the 100 mS m^{-1} batch, stored in 500 mL DURAN glass bottles, was initial monitored approximately every 2 weeks, followed by a verification at near the end of its shelf life, showing no significant trends as a function of storage time (slope: 1×10^{-8} S m^{-1} week^{-1}) (Fig. 3b). The long-term stability of the 10 S m^{-1} batch was monitored every 6 months, also showing no significant change in electrolytic conductivity with time (slope: 1×10^{-5} S m^{-1} week^{-1}) (Fig. 3d).

All prepared reference materials showed a high degree of stability over their shelf lives, with no significant, systematic trend in electrolytic conductivity values as a function of time stored at room temperature, away from direct sunlight. Electrolytic conductivity of individual RM bottles within a batch did not vary outside measurement uncertainty (standard uncertainty $E_N < 1$) as a function of time. As such, no uncertainty contribution specifically for long-term stability could be separated from measurement uncertainty. Previously [9, 15], relative drift tolerances as a function of time were assigned to individual RM conductivity level: ± 0.15 % for 10 mS m^{-1}, and ± 0.08 % for 100 mS m^{-1}, 1 S m^{-1}, and 10 S m^{-1}. Based on the information presented here, no evidence was found to show that these assigned tolerances were not acceptable. Long-term stability with storage at room temperature is similar to stability levels reported for a variety of other electrolytic conductivity CRMs in the literature [11–14, 18, 19].

Stability in lower conductivity CRMs: 10 mS m^{-1}

A 22-kg batch of electrolytic conductivity reference material, with a nominal conductivity value of 10 mS m^{-1}, was produced and bottled into 500-mL DURAN or Kimble glass bottles, sealed with Parafilm. The reference material was manufactured to investigate:

1. potential influence on electrolytic conductivity related to bottling and storage in DURAN vs. Kimble glass,
2. influences of transportation (e.g., shipment by air freight) and conditions potentially encountered during shipment of CRMs (e.g., higher temperatures), and
3. the long-term stability of this lower conductivity reference material over a 1-year period, twice its suggested shelf life.

Short-term stability and transport conditions

Homogeneity

According to ISO Guide 35 [8], the measurement of 3 bottles, from a batch of 21 bottles, within a short time period (here, less than 1 week) additionally constitutes a homogeneity study. The 22 kg 10 mS m^{-1} batch was divided into a total of 42 bottles (500 mL), 21 DURAN glass and 21 Kimble glass bottles; 3 bottles of each type were selected at random and electrolytic conductivity measured to (1) assign the reference value to the batch, and (2) perform a homogeneity study on each sub-group of bottles. Table 3 gives the values measured on each bottle, with standard (characterization) uncertainties of 0.005 5 mS m^{-1}. All values are identical within measurement uncertainty, showing no difference between replicates, nor between bottle types. The 22-kg batch of reference material showed no inhomogeneity.

The batch reference value, from repeat measurements performed on 6 of 42 bottles, was determined to be 9.972 mS m^{-1}, with an expanded uncertainty ($k=2$) of 0.021 mS m^{-1} at 25 °C, with typical 10 mS m^{-1} electrolytic conductivity CRM inclusions for homogeneity and stability.

Effect of transport

Two pairs of DURAN and Kimble bottles were shipped from Denmark to Canada and shipped back, un-opened, by air freight, a distance of 7200 km, each way. Bottles were sealed in the usual manner (i.e., cap tightly sealed and wrapped in Parafilm) and packaged in Styrofoam shells for shipping. No special precautions were taken for pressure, humidity, or temperature changes during transportation. Shortly after the bottles' return to DFM, a pair of bottles, one DURAN and one Kimble glass, were tested (Table 4). No change in electrolytic conductivity was observed as a result to transportation, nor was any differentiation seen between the two bottle types. The second pair of bottles were stored in a refrigerator (5 °C) for 1 month, to simulate a hypothetic condition encountered in a laboratory setting: storage under refrigerated conditions before opening and use.

Table 4 Electrolytic conductivity (mS m^{-1}) at 25 °C of a reference material batch (nominal conductivity: 10 mS m^{-1}) subject to short-term storage and transport conditions, for RM storage in two different types of glass bottle: DURAN and Kimble

	Electrolytic conductivity (mS m^{-1})	
	DURAN	Kimble
Air-freight shipping	9.971	9.971
Storage: 3 days		
Stored in direct sunlight	9.972	9.971
(2 bottles)	9.971	9.974
5 °C	9.971	9.975
30 °C	9.971	9.973
40 °C	9.974	9.974
(2 bottles)	9.976	9.977
Storage: 1 month		
Stored in direct sunlight[a]	9.980	9.974
5°C[b]	9.977	9.975
30 °C	9.975	9.978
Storage: 4 months + 3 months without Parafilm	9.971	9.975

[a] *Storage conditions* 3 days under refrigeration (5 °C), followed by 1 month in direct sunlight

[b] *Treatment* air-freight shipping, followed by 1 month stored at 5 °C

Short-term storage

ISO 17034 [7], with further specifications in ISO Guide 35 [8], requires producers of CRMs to verify the stability of materials under a range of conditions potentially encountered during transportation and short-term storage at recipient's facility prior to use, in order to provide recommendations for transportation. A prior report on short-term stability of a 0.15 mS m^{-1} CRM has focused on ascertaining CRM stability under extreme conditions (i.e., 50 °C over 7 days to 21 days) [13]. Here, a variety of potential transport and short-term storage related conditions are explored, as summarized in Table 4. Very short-term (i.e., 3 days) storage at 5 °C, 30 °C, and 40 °C (see Fig. 4), as well as room-temperature (in direct sunlight) and longer-term storage without Parafilm sealing, did not influence reference material electrolytic conductivity, showing no differentiation between storage in DURAN and Kimble glass bottles.

Stability of electrolytic conductivity materials under refrigerated conditions (3 days and 1 month) is in contrast to Barron and Ashton [12], who reported instability of low conductivity CRM within less than 2 weeks of storage at 4 °C, but in agreement with Fraga et al. [13], who reported stability of another low conductivity CRM over 57 weeks of storage at 4 °C, while stability at elevated temperatures (30 °C and 40 °C) is consistent with that reported previously for other reference materials (50 °C, 21 days) [13].

Exposure to direct sunlight is generally recommended against, due to potential growth of biological contaminants, degradation of CRM contents, or increased evaporation under higher-temperature conditions, likely as a result of solar heating. However, no prior reports exist, to the best of our knowledge, on the exposure of electrolytic conductivity reference materials, consisting of inorganic salt (KCl) and UV-treated and filtered ultra-pure water (i.e., unlikely to contain biological contaminants). Exposure of 2 pairs of bottles, one DURAN and one Kimble glass, to 3 days, as well as 1 month, of strong incident sunlight (summer months, southern exposure in Denmark) in a non-temperature-controlled room, did not result in any significant change in electrolytic conductivity value (Table 4).

CRM bottles are typically wrapped with Parafilm around the cap and neck joint upon bottling and remain so until used for the first time. To investigate the longer-term potential influence of the presence/absence of Parafilm, two bottles, one of each glass composition, were held under recommended storage conditions: for 3 months with Parafilm, followed by 4 months without. Following storage of a total of 7 months, 7 month beyond the recommended lifetime of the 10 mS m^{-1} RM, the conductivity values were found not to

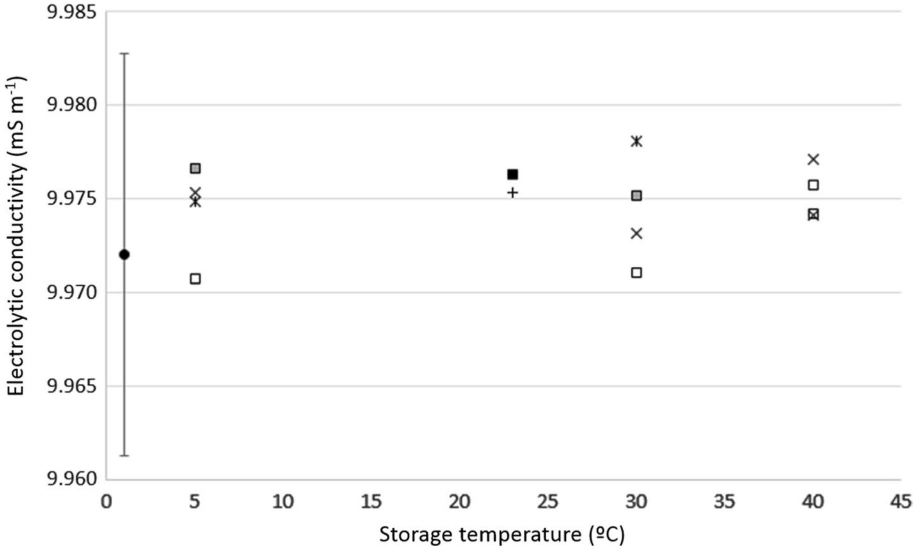

Fig. 4 Electrolytic conductivity (note scale: in mS m^{-1}) of solutions, stored in DURAN (open square, grey square, filled square) and Kimble (×, *, +) glass bottles, at various temperatures: 5 °C (3 days and 1 month), 23 °C (3 months), 30 °C (3 days and 1 month), and 40 °C (3 days and 1 month). Storage duration is indicated as flows: 3 days (open square, ×), 1 month (grey square, *), and 3 months (filled square, +). Batch value (filled circle, standard uncertainty indicated) = electrolytic conductivity value assigned to entire batch, from evaluation of both DURAN and Kimble glass bottles, with standard uncertainty typically assigned to 10 mS m^{-1} CRMs (including homogeneity and stability)

have changed significantly. As an increase in conductivity values was not observed (Table 4), this suggests that (a) sealing of both DURAN and Kimble glass bottles was sufficient to prevent significant evaporation of water, and (b) leaching of ions from the glass bottles was insignificant.

Monitoring study: long-term stability and bottle type

From the same 22-kg batch of 10 mS m^{-1} reference material, sufficient bottles of each type (DURAN and Kimble borosilicate glass) were set aside in order to perform a monitoring study, investigating any potential influence of bottle composition on the long-term stability of this RM. Electrolytic conductivity of reference material stored in pairs of DURAN and Kimble glass bottles, at room temperature (23.0 °C ± 0.5 °C) away from direct sunlight, was evaluated every 3 months over the course of 1 year: the 6-month shelf life + an additional 6 months (Table 5).

Electrolytic conductivity after the recommended shelf life (6 months) showed the RM to be stable in bottles of both glass compositions. This can be seen graphically in Fig. 5, where electrolytic conductivity as determined in DURAN and Kimble glass bottles (values given in Table 5) falls within standard uncertainty of the batch reference value assigned to the RM. These results reveal no influence on long-term stability related to slight differences in borosilicate composition between the two brands of 500-mL glass bottles.

Table 5 Electrolytic conductivity (mS m^{-1}) at 25 °C of a reference material batch (nominal conductivity: 10 mS m^{-1}) as a function of time elapsed

Time elapsed (months)	Electrolytic conductivity (mS m^{-1})	
	DURAN	Kimble
3	9.976	9.975
6	9.976	9.976
	9.975	9.977
9	9.978	9.977
	9.974	9.976
12	9.976	9.976
	9.975	9.978

Conclusions

This work has focused on aspects of ISO 17034:2016 and ISO Guide 35:2017, as applied to the production of certified reference materials (CRMs) for use as electrolytic conductivity standards at the Danish National Metrology Institute (NMI): DFM A/S. The selection of bottling material, and volume, i.e., 500-mL borosilicate glass bottle, was shown to be appropriate. These bottles demonstrated the highest degree of long-term stability over the lifetime of a 100 mS m^{-1} electrolytic conductivity solution. Further, different brands of 500 mL borosilicate glass bottles were shown to impart no influence on 10 mS m^{-1} reference

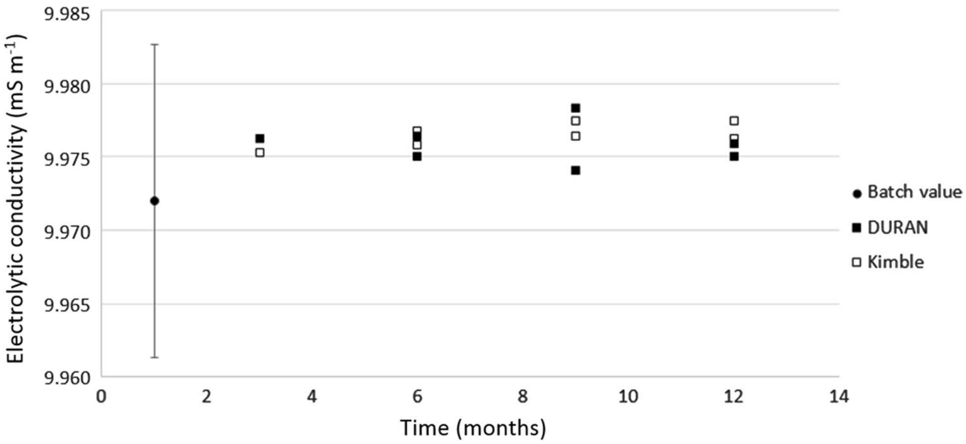

Fig. 5 Electrolytic conductivity (note scale: in mS m^{-1}) of solutions, stored in DURAN (grey square) and Kimble (open square) glass bottles, at 23 °C for 3 months to 12 months. Batch value (filled circle, standard uncertainty indicated) = electrolytic conductivity value assigned to entire batch, from evaluation of both DURAN and Kimble glass bottles, with standard uncertainty typically assigned to 10 mS m^{-1} CRMs (including homogeneity and stability)

material characterization value, homogeneity, short- or long-term stability (1 year).

Four electrolytic conductivity level CRMs (10 mS m^{-1} to 10 S m^{-1}) were shown to have acceptable long-term stability, over their shelf lives and beyond, when stored under laboratory conditions. Focus was placed on short-term stability studies, and the influence of transport, and their potential influence on the electrolytic conductivity values of bottled 10 mS m^{-1} reference material. Potential influence of air freight (transport), as well as storage under a variety of conditions (potentially encountered during transport: direct sunlight, refrigeration, and high temperatures (30 °C and 40 °C)) was shown to have no influence on measured electrolytic conductivity values. These results demonstrate that bottling material, suggested storage conditions, and packaging material (employed during transport from CRM production facility to client) are adequate to guarantee the validity of CRM reference value for electrolytic conductivity, within CRM uncertainty (including homogeneity and stability).

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