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# MOLALITY-BASED PRIMARY STANDARDS OF ELECTROLYTIC CONDUCTIVITY

(IUPAC Technical Report)

*Prepared for publication by*

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# Molality-based primary standards of electrolytic conductivity

## (IUPAC Technical Report)

*Abstract:* New values of electrolytic conductivity were determined for aqueous KCl solutions with molalities of 0.01, 0.1, and 1.0 mol/kg in the temperature range 0 to 50 °C, at 5 K intervals. Expanded uncertainties,  $2u_c$ , were also calculated in accordance with the presently accepted protocol for the treatment of uncertainty. The new conductivity values are recommended as primary standards of electrolytic conductivity based on molality. They replace the previous values, based on the nonstandard demal scale, which were determined only at 0, 18, and 25 °C. The accuracy of the technique used was evaluated by repeating the determination of the previously recommended demal-based IUPAC standards of electrolytic conductivity and through comparison with other absolute measurements.

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### 1. INTRODUCTION

The existing primary standards of electrolytic conductivity are based on measurements of Jones and Bradshaw [1]. These standards consist of solutions of a defined concentration on the so-called demal scale, which is used only for electrolytic conductivity. Parker and Parker [2] first introduced the expression demal "...to indicate concentrations which are expressed in equivalents per cubic decimeter. To take the place of the word 'normal', the expression '*demal*' is suggested." Parker and Parker calculated the corresponding apparent masses of KCl and of H<sub>2</sub>O (at 0 °C), uncorrected for air buoyancy, for 0.01, 0.1, and 1.0 demal solutions. Masses (corrected for air buoyancy), calculated based on the atomic weights of 1933, were later recommended by Jones and Bradshaw: 0.745 263, 7.419 13, and 71.1352 g, per kilogram of aqueous solution, for the 0.01, 0.1, and 1.0 demal solutions, respectively [1]. These mass values have been retained through the present day [3,4]. The designations 0.01, 0.1, and 1.0 demal are retained in the present work, solely with reference to comparisons with previous measurements, to refer to these respective solutions as defined by Jones and Bradshaw.

The demal scale suffers from lack of a direct relationship to the generally recognized units of concentration or molality accepted by IUPAC and generally used in solution chemistry. The original measurements of Jones and Bradshaw were performed over 60 years ago, and several basic standards have been changed since that time. Of specific interest to the present work are those of temperature, resist-

ance, and the atomic weights of K and Cl. Hence, the original values of Jones and Bradshaw had to be corrected in order to obtain the primary standards of electrolytic conductivity that are presently accepted by the Organisation Internationale de Métrologie Légale (OIML) [3] and recommended by IUPAC [4]. In addition, the current primary standards [3,4] are available only for three temperatures, i.e., 0, 18, and 25 °C.

The demal scale was envisioned by Jones and Bradshaw [2] as a scale defined strictly by mass, such that future changes in the atomic weights  $A_r(\text{K})$  of K and  $A_r(\text{Cl})$  of Cl or in the litre would not affect the actual electrolytic conductivity. This definition also avoided “the numerous and well-known errors in volumetric procedure” [2]. These factors had all affected the electrolytic conductivity of the prior, volume-based standards, which were referred to the amount-of-substance concentration of KCl (mol KCl per litre solution). Since that time, the relative uncertainties of  $A_r(\text{K})$  and  $A_r(\text{Cl})$  have been reduced to 0.0026% and 0.0025%, respectively [5], primarily due to the development of mass spectrometry. These present values are now significantly lower than the attainable precision of the measurement of electrolytic conductivity. Hence, it is again feasible to reestablish the primary standards of electrolytic conductivity on an amount-of-substance basis, e.g., molality, without the concern that future changes in the atomic weights would significantly affect the primary standard values of electrolytic conductivity.

Recently, absolute determinations of electrolytic conductivity have been performed at the National Institute of Standards and Technology (NIST), USA, of solutions of known molality in the temperature range 0 to 50 °C at intervals of 5 K [6–8]. These determinations were performed using a conductivity cell with a well-defined geometry. The cell constant was determined via accurate mechanical measurement of a removable, straight center tube. Other experimental parameters (notably temperature, resistance, and amount of substance) affecting the final recommended value were determined with reference to the present fundamental units. Measurements of the previous demal-based standards of electrolytic conductivity were also performed using the same cells [6,8,9] in order to demonstrate agreement with the previous standards.

The present article presents, in a concise form, the results of our conductivity measurements along with the analysis of the component uncertainties of the values recommended for the electrolytic conductivity of the molality-based primary standards.

## 2. FUNDAMENTALS

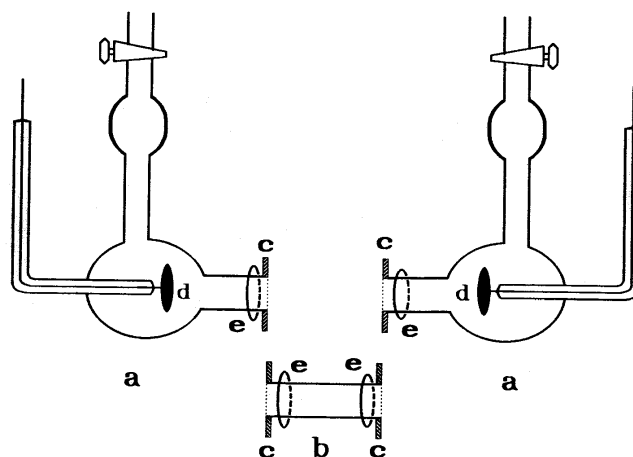
The fundamentals of the electrolytic conductivity measurement and the cell construction are described here. Further details are given in the original references [6–8].

### 2.1 Conductivity measurements for the aqueous solutions of KCl of molality 0.01 and 0.1 mol/kg

Conductivity measurements for the new primary standards of molality 0.01 and 0.1 mol/kg [6,7] were performed in a Jones-type cell with a removable center extension tube. The cell is depicted in Fig. 1. The measurements were performed using an *ac* Jones bridge [10] at frequencies,  $f$ , equal to 1, 2, and 5 kHz. Then, the resistance indicated at balance of the bridge was extrapolated to  $f = \infty$ . The resistances were determined in this manner using the cell with (W) and without (N) the center extension tube, for each primary standard solution at each temperature. These measurements yielded the resistances  $R_W$  and  $R_N$ , respectively, given by eqs. 1 and 2:

$$R_W = \frac{K_W}{\kappa}, \quad (1)$$

$$R_N = \frac{K_N}{\kappa} \quad (2)$$



**Fig. 1** Diagram of the *ac* conductivity cell used for the absolute measurements: **a**, **a** – end sections (half cells); **b** – center extension tube; **c**, **c** – flanges; **d**, **d** – Pt electrodes; **e** – o-rings. A plastic band (not shown) surrounds the outer circumference of the mating flanges to hold them coaxially and a compression clamp (also not shown) presses on the o-rings to hold the mating flanges together.

where  $K_W$  and  $K_N$  are the corresponding cell constants and  $\kappa$  is the conductivity.

The length,  $l$ , and cross-sectional area,  $A$ , of the center extension tube were determined mechanically. Hence, the cell constant of the tube,  $K_T = l/A$ , can be calculated. It is equal to  $K_W - K_N$ . Thus,

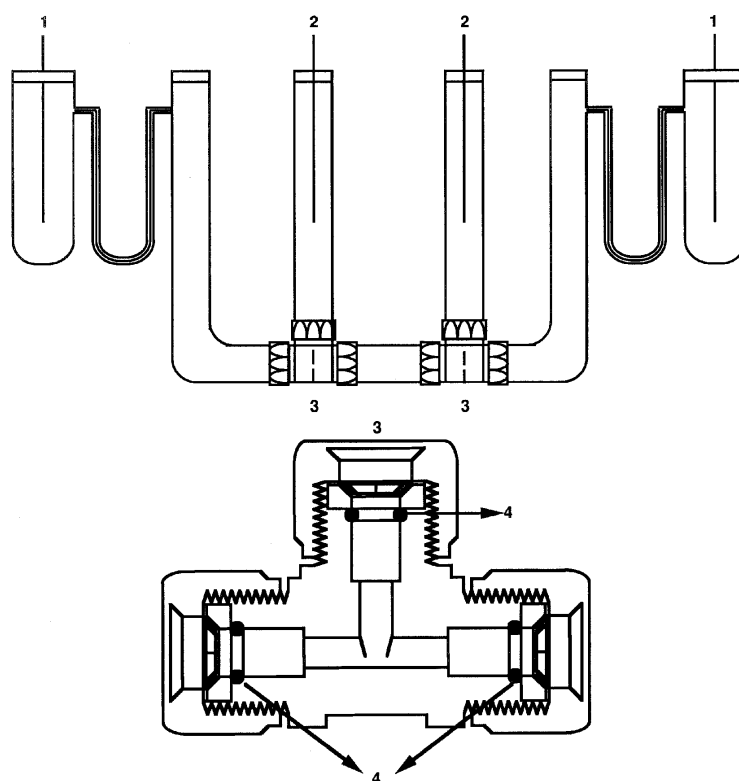
$$\kappa = \frac{K_W - K_N}{R_W - R_N} = \frac{l/A}{R_W - R_N} \quad (3)$$

Each quantity in the right-hand side of eq. 3 is known either by mechanical or electrical measurement. Therefore,  $\kappa$  is absolutely determined.

## 2.2 Conductivity measurements for aqueous solution of KCl of molality 1.0 mol/kg

Conductivity measurements for the new primary standard for the aqueous solution of KCl of molality 1.0 mol/kg [8] were performed using a four-electrode *dc* cell. The cell is depicted in Fig. 2. For the *dc* cell, a piece of straight, precision bore glass tubing (nominal diameter, 1.0 cm) was cut into three sections that were assembled end-to-end in the assembled cell. This assembly, thus, had four edges: one at the outer end of each of the side sections and two at the joints with the center tube. A separate section of glass tubing was placed perpendicular to the axis of the precision tubing at each of these edges using a plastic joint to hold it tightly. The dimensions of the center tube were accurately measured. The entire cell, including the perpendicular tubes, was filled with the primary standard solution. A Ag|AgCl electrode was placed in each of the four perpendicular tubes.

The measurement procedure was the same as that for a four-terminal *dc* resistance measurement. The center pair of electrodes was used to measure the potential drop across the center tube via the two narrow gaps (ca. 25  $\mu\text{m}$ ) between the center tube and the side tubes. The outer electrode pair was used for the current electrodes. Concentration polarization and undesired side reactions were eliminated using Ag|AgCl electrodes as the current electrodes. In order to measure  $\kappa$  for a given primary standard, the potential difference between the two center Ag|AgCl electrodes was measured after applying a constant current,  $i$ , to the outer current electrodes. Any difference between the standard potentials,  $E^\circ$ , of the potential difference-sensing electrodes was eliminated by reversing the direction of  $i$  and averaging



**Fig. 2** Diagram of the *dc* conductivity cell used for the absolute measurements: **1, 1** – current electrodes; **2, 2** – potential difference sensing electrodes; **3** – Nylon tee joints; **4, 4** – o-rings.

the magnitudes of the two measured potential differences. The averaged potential difference,  $\Delta E$ , obtained in this manner was related to the electrolytic conductivity of the solution by eq. 4

$$\kappa = \frac{K_T}{R_T} = \frac{iK_T}{\Delta E}, \quad (4)$$

where  $R_T$  is the resistance of the solution in the center tube and  $\kappa$  and  $K_T$  are as defined for the *ac* cell. The value of  $i$  was determined by measuring the potential drop across a primary standard resistor, used in the four-terminal mode.

The choice between the *ac* or *dc* measurement procedure was dictated by the overall combined uncertainty that could be attained with the given procedure. The combined uncertainty, in turn, was governed by the optimal measured potential differences and by practical values of  $K$ , which were limited by the dimensions of the temperature baths used.

### 3. RECOMMENDED VALUES

The recommended electrolytic conductivities for the three primary standards, i.e., aqueous solutions of KCl of molality 0.01, 0.1, and 1.0 mol/kg, are given in Table 1. Conductivities and their uncertainties in this and subsequent tables are presented in  $\mu\text{S}/\text{cm}$  ( $=10^{-4}$  S/m). These recommended values were calculated using eq. 5,

$$\kappa/\kappa^0 = a + b(t/t^0) + c(t/t^0)^2 + d(t/t^0)^3 \quad (5)$$

a third-order polynomial fit of the measured values, where  $a$ ,  $b$ ,  $c$ , and  $d$  are the parameters in the polynomial fit,  $t$  is the Celsius temperature on the ITS-90,  $t^0 = 1\text{ }^\circ\text{C}$  is a standard temperature, and  $\kappa^0 = 1\text{ S/m}$  is a standard conductivity.

The values of the parameters  $a$ ,  $b$ ,  $c$ , and  $d$  are given in Table 2 for each of the three molalities of the new primary standards.

**Table 1** Recommended electrolytic conductivities,  $\kappa$  ( $\text{H}_2\text{O}$  corrected), for different KCl molalities, with expanded uncertainties,  $2u_c$ . The Celsius temperature,  $t$ , is on the ITS-90.

$t$ , $^\circ\text{C}$	$10^4 \kappa / \text{S m}^{-1}$						$\text{H}_2\text{O}$ ( $\text{CO}_2$ saturated)
	$m(\text{KCl}) = 0.01$ mol/kg		$m(\text{KCl}) = 0.1$ mol/kg		$m(\text{KCl}) = 1.0$ mol/kg		
	Value	$2u_c$	Value	$2u_c$	Value	$2u_c$	
0	772.92	0.23	7116.85	2.85	63 488	25	0.58
5	890.96	0.27	8183.70	3.27	72 030	29	0.68
10	1013.95	0.30	9291.72	3.72	80 844	32	0.79
15	1141.45	0.34	10 437.1	4.2	89 900	36	0.89
18	1219.93	0.37	11 140.6	4.5	–	–	0.95
20	1273.03	0.38	11 615.9	4.6	99 170	40	0.99
25	1408.23	0.42	12 824.6	5.1	108 620	43	1.10
30	1546.63	0.46	14 059.2	5.6	118 240	47	1.20
35	1687.79	0.51	15 316.0	6.1	127 970	51	1.30
40	1831.27	0.55	16 591.0	6.6	137 810	55	1.40
45	1976.62	0.59	17 880.6	7.2	147 720	59	1.51
50	2123.43	0.64	19 180.9	7.7	157 670	63	1.61

**Table 2** Parameters in the third-order polynomial fit<sup>a</sup> for electrolytic conductivity,  $\kappa$ , for each KCl molality.

Molality, mol/kg	Parameters			
	$a$	$b$	$c$	$d$
0.01 <sup>b</sup>	$7.729\ 21 \times 10^{-2}$	$2.308\ 46 \times 10^{-3}$	$1.077\ 15 \times 10^{-5}$	$-5.840\ 94 \times 10^{-8}$
0.1 <sup>b</sup>	0.711 685	$2.090\ 02 \times 10^{-2}$	$8.991\ 44 \times 10^{-5}$	$-5.071\ 24 \times 10^{-7}$
1.0	6.348 82	0.167 913	$6.007\ 81 \times 10^{-4}$	$-3.837\ 02 \times 10^{-6}$

<sup>a</sup>Equation 5:  $\kappa/\kappa^0 = a + b(t/t^0) + c(t/t^0)^2 + d(t/t^0)^3$

<sup>b</sup>Parameters presented here for the aqueous solutions of KCl of molality 0.01 and 0.1 mol/kg are recalculated (see text) from the original values [7] referred to the IPTS-68 for the Celsius temperature.

The values in Table 1 were corrected for the electrolytic conductivity of the solvent, i.e., water in equilibrium with atmospheric  $\text{CO}_2$ , at the temperature of measurement. The measured conductivities of the solvent are given in the rightmost column of Table 1. This solvent conductivity is subtracted from the value measured for the test solution (not shown) to yield the reported conductivity,  $\kappa$ , at the given molality and Celsius temperature.

The measurements for the aqueous solutions of KCl of molality 0.01 mol/kg and 0.1 mol/kg were originally performed using a quartz thermometer calibrated according to the IPTS-68. These measurements were subsequently recalculated to the ITS-90, adopted on 1 January 1990, as follows. For the

temperature range from 0 to 50 °C, the relationship between  $t$  on the ITS-90 and  $t_{68}$ , the Celsius temperature on the IPTS-68, is given by

$$t - t_{68} = 2.68 \times 10^{-4} t. \quad (6)$$

The correction was performed using eq. 7, where  $\kappa$  is the corrected electrolytic conductivity (ITS-90),  $\kappa_{68}$  is the originally measured conductivity (IPTS-68), and  $b_{68}$ ,  $c_{68}$ , as well as  $d_{68}$  are the parameters from the originally published polynomial fit [7]:

$$\kappa/\kappa^0 = \kappa_{68}/\kappa^0 + \left[ b_{68} + 2c_{68}\left(t/t^0\right) + 3d_{68}\left(t/t^0\right)^2 \right] 2.6 \times 10^{-4} \left(t/t^0\right) \quad (7)$$

Subsequent measurements of  $\kappa$  at 25 and 40 °C, performed using the thermometer calibrated on the ITS-90, yielded results consistent to within 0.01% of the corresponding corrected values. With these measurements, the correction procedure described above was verified.

Values of the parameters presented in Table 2 for the aqueous solutions of KCl of molality 0.01 and 0.1 mol/kg were also recalculated by substituting eq. 6 into eq. 7 and gathering the constant ( $t$ -independent) terms together for each term of the resulting third-order polynomial. This calculation yields eqs. 8–11 for the parameters  $a$ ,  $b$ ,  $c$ , and  $d$  on the ITS-90:

$$a = a_{68} \quad (8)$$

$$b = b_{68}(1 - 2.6 \times 10^{-4})^{-1} \quad (9)$$

$$c = c_{68}(1 - 2.6 \times 10^{-4})^{-2} \quad (10)$$

$$d = d_{68}(1 - 2.6 \times 10^{-4})^{-3}. \quad (11)$$

The values recalculated from eqs. 8–11 are presented in Table 2. The values of  $\kappa$  calculated using these parameters are identical to those originally published [7]. The original conductivities were calculated using eq. 7.

Subsequent to the change from the IPTS-68 to the ITS-90, the  $dc$  measurements for the aqueous solution of KCl of molality 1.0 mol/kg were performed. Hence, no correction was required.

The original calculations performed using eqs. 5 and 7 were also verified using the published values of  $a$ ,  $b$ ,  $c$ , and  $d$  (converted to the ITS-90) given in Table 2. In all cases, the rounded error was well below the recommended uncertainty. The only change made in the values, as presented in Table 1, was that for  $t = 0$  °C for the aqueous solution of KCl of molality 1.0 mol/kg. The original value in [8] contained a typographical error: the smoothed value 0.063 487 S/cm is corrected here to 0.063 488 S/cm. In addition, those conductivities for the aqueous solution of KCl of molality 0.01 mol/kg originally given to the third place after the decimal point have been rounded to the second place, in order to reflect the stated uncertainty.

#### 4. UNCERTAINTIES

The expanded combined uncertainties,  $U = 2u_c$ , of the recommended electrolytic conductivities are listed in Table 1. The combined uncertainties,  $u_c$ , were calculated from component uncertainties,  $u_i$ , according to the International Organization for Standardization (ISO) protocol [11]. Original uncertainties, reported as 95% confidence intervals, were divided by 2 to yield the values of  $u_i$  presented below. In all other cases, a uniform probability distribution was assumed and the original value was divided by  $3^{1/2}$  to yield the corresponding  $u_i$  presented below. These  $u_i$  values were then combined in quadrature (square root of the sum of the variances) to obtain the  $u_c$  value for each solution. Uncertainties given as percentages are on a relative basis.

Each recommended value has two Type A components of  $u_i$ . The first Type A component corresponds to the difference between the smoothed  $\kappa$  value (calculated from eq. 5) and the individual, discrete  $\kappa$  values measured at the given temperatures. The corresponding  $u_i$  values are 0.0046%, 0.0126%, and 0.0145% for the 0.01, 0.1, and 1.0 mol/kg primary standards, respectively.

The second Type A component of  $u_i$  in the overall uncertainty was that of the measurement of  $K_T$  for the center tube. This measurement was based on mechanical measurement of the length,  $l$ , and inside diameter,  $d$ , of the tube.  $K_T$  and the corresponding  $u_i$  for the *ac* measurements (0.01 and 0.1 mol/kg primary standards) were  $10.0585 \text{ cm}^{-1}$  and  $0.00065 \text{ cm}^{-1}$  (0.0065%), respectively.  $K_T$  and the corresponding  $u_i$  for the *dc* measurements were  $31.195 \text{ cm}^{-1}$  and  $0.0027 \text{ cm}^{-1}$  (0.0085%), respectively. For both measurements, the dominant  $u_i$  calculated for  $K_T$  was the uncertainty in the measurement of  $d$  of the given tube. Measurements of  $d$  were performed at each of three angular positions along the tube at three (*ac* cell) or four (*dc* cell) locations along the cell axis from  $x = 0$  to  $x = l$ , making a total of 9 (*ac* cell) or 12 (*dc* cell) measurements. The value of  $l$  was measured for both cells at each of four positions spaced by  $\pi/2$  ( $90^\circ$ ) around the circumference of the center tube, making a total of four measurements of  $l$  for each cell. The reported Type A components of  $u_i$ , noted above for each tube, represent the propagated  $u_i$  of the calculated  $K$  attributable to the corresponding sets of measurements.

The Type B components of  $u_i$  in the overall uncertainty are outlined in the following paragraphs.

The effect of variations of the cell temperature on  $K_T$  may be calculated using eq. 12 from the linear expansion coefficient,  $\alpha_g$ , of the borosilicate glass used for its construction:

$$\frac{1}{K_{\text{cell},T}} \frac{dK_{\text{cell},T}}{dt} \approx \frac{1}{l} \frac{dl}{dt} - \frac{1}{A} \frac{dA}{dt} = \alpha_g - 2\alpha_g = -\alpha_g \quad (12)$$

Equation 12 applies to both the *ac* and *dc* measurement, since the geometry and construction materials of both center tubes are the same. For the *ac* measurements (0.01 and 0.1 mol/kg standards),  $\kappa$  for each molality was calculated using the corrected value of  $K_T$  for each  $t$  value using  $\alpha_g = 3.6 \times 10^{-6} \text{ K}^{-1}$  for borosilicate glass [12]. The maximum correction calculated from eq. 12 was 0.009% and occurred at both 0 and  $50^\circ\text{C}$ . The uncertainty in this correction is negligible in the overall uncertainty calculation. For the *dc* measurements, the single value of  $K_T$  noted above was used at all  $t$  values. No correction was made for the variation of the  $K_T$  with  $t$ . The value  $u_i = 0.0052\%$  was taken for the resulting  $u_i$  applicable to  $K_T$  for the *dc* measurements, based on the estimated change of  $K_T$  with temperature.

The effect of the uncertainty of the bath temperature was calculated using the temperature coefficient of  $\kappa$  for each temperature and the uncertainty in  $t$ . The temperature coefficient was determined directly from the smoothed polynomial of  $\kappa$  vs.  $t$  noted above. The uncertainty in the measurement of  $t$ , arising from the calibration of the thermometer, was  $u_i = \pm 0.002 \text{ K}$ . It was taken as a uniform probability interval for the calculation of the respective  $u_i$  values in  $\kappa$ .

The solute KCl for all the primary standards was a NIST Standard Reference Material (SRM) 999, heated in air for 4 h at  $500^\circ\text{C}$  to expel occluded water. It was stored in a desiccator over anhydrous  $\text{Mg}(\text{ClO}_4)_2$  before use. The certified assay of this SRM was based on coulometric argentometric titration for Cl and on gravimetric assay for K [13]. The assayed purity of this material after heating was 99.986%. All certified impurities in this SRM were cationic or anionic species. The molar electrolytic conductivities of all substances present at a mass fraction exceeding  $10 \mu\text{g/g}$  are within 10% of the molar electrolytic conductivities of the  $\text{K}^+$  and  $\text{Cl}^-$  ions. Hence, no correction for the certified assay was made in the gravimetric preparation of the primary standard solutions. The estimated  $u_i$ , equal to 0.0025%, represents the best estimate of the net second-order effect of the difference attributable to these impurities.

Evaporation of the primary standard solutions during transfer to the conductivity cell resulted in a corresponding  $u_i$  estimated as 0.0025%.



The value of  $u_i$  for the electrical measurement of resistance for the *ac* measurements of the 0.01 and 0.1 mol/kg primary standard solutions was 0.000 57%. This value included the uncertainty due to correction for the lead resistance. The corresponding  $u_i$  for the measurements of current and potential in the *dc* measurement for the 1.0 mol/kg solution was 0.000 61%. This latter estimate takes into account both the uncertainty of the measurement of  $\Delta E$  and that of the measurement of  $i$  (determined from the potential drop across a four-terminal standard resistor calibrated against the primary standard of resistance).

The uncertainty of the correction for the electrolytic conductivity of the water solvent was  $2 \times 10^{-6}$  S/m, equal to 1% of the net correction. This uncertainty corresponded to a  $u_i$  for the corrected electrolytic conductivity of less than 0.0015% in all cases.

The maximum values of  $2u_c$ , calculated using the Type A and Type B components of  $u_i$  described above and the method of root sum of squares, are 0.025%, 0.034%, and 0.037% for the 0.01, 0.1, and 1.0 mol/kg primary standards, respectively. A conservative estimate of 0.03% relative was uniformly applied to the recommended values in Table 1 for the 0.01 mol/kg primary standard. An estimate of 0.04% relative was uniformly applied for the 0.1 and 1.0 mol/kg primary standards in order to obtain the recommended expanded uncertainties presented in Table 1.

## 5. COMPARISON OF THE PRESENT AND PREVIOUS STANDARDS AND MEASUREMENTS

Consistency of the metrological procedure used herein was demonstrated by repeating measurements for the previously recommended 0.01, 0.1, and 1.0 demal standards using the identical cells and equipment used for the molality-based primary standards [8,9]. These results are presented in Table 3, together with the primary standard values accepted by OIML [3] and recommended by IUPAC [4]. The maximum deviation of the present results from the OIML values is 0.027%. This deviation lies within the recommended uncertainty of the molality-based primary standards described above. In Table 3, the  $\kappa_{68}$  values are referred to  $t$  values on the IPTS-68 in order to facilitate comparison with the previous standards, as originally presented. The conductivities determined from the present *dc* measurements for the

**Table 3** Conductivities,  $\kappa_{68}$ , determined by absolute measurements, and the previously accepted OIML demal-based values (based on IPTS-68).

Primary standard	$t/^\circ\text{C}$ (IPTS-68)	$10^4 \kappa_{68} / \text{S m}^{-1}$					
		This work [8,9] <sup>a,b</sup>		OIML standard [3,4] <sup>c</sup>		Saulnier and Barthel [13] <sup>d</sup>	
		Value	Uncert.	Value	Uncert.	Value	Uncert.
0.01 demal	0	773.09	0.23	773.3	0.77	773.1 <sub>7</sub>	0.23
	18	1220.1	0.37	1220.1	1.2	1220.7 <sub>6</sub>	0.37
	25	1408.4	0.42	1408.3	1.4	1409.3 <sub>6</sub>	0.42
0.1 demal	0	7134.6	2.9	7134.0	7.1	–	–
	18	11 161	4.5	11 163	11	–	–
	25	12 851	5.1	12 852	13	–	–
1.0 demal	0	65 135	26	65 140	65	–	–
	18	97 811	39	97 810	97	–	–
	25	111 303	45	111 310	111	–	–

<sup>a</sup>Values recalculated to IPTS-68 for this table only.

<sup>b</sup>Relative uncertainty equals 0.03% for 0.01 demal solution, 0.04% for 0.1, and 1.0 demal solutions.

<sup>c</sup>Tabulated uncertainty calculated using estimated relative uncertainty of 0.1% at a 99% confidence level [4].

<sup>d</sup>Tabulated uncertainty calculated using estimated relative uncertainty of 0.03% [14].

1.0 demal solution were converted from the ITS-90 to the IPTS-68 using eq. 7 (solved for  $\kappa_{68}$ ) and the parameters for the third-order polynomial for the 1.0 demal solution published in the original work [8].

The conductivities for the 0.01 demal solution determined in the present work are also in agreement or near agreement with values for the 0.01 demal primary standard solution, as measured in a separate absolute measurement by Saulnier and Barthel [14]. These values are also presented in Table 3. The most recent estimate of the uncertainty of these determinations is  $u_i = \pm 0.03\%$  [15].

No uncertainty was assigned to the original absolute values of Jones and Bradshaw [1], which were determined by a chain of at least three separate Jones-type cells with optimized  $K$  values. A modern estimate of the uncertainty in the Jones and Bradshaw values is  $u_i = \geq 0.02\%$  [6].

## 6. LIST OF SYMBOLS AND ABBREVIATIONS

$A$	cross-sectional area, $\text{m}^2$
$A_r(\text{K})$	atomic weight (relative atomic mass) of potassium
$A_r(\text{Cl})$	atomic weight (relative atomic mass) of chlorine
$a, b, c, d$	parameters in polynomial fit of $\kappa$ vs. $t$ (ITS-90) (eq. 5)
$a_{68}, b_{68}, c_{68}, d_{68}$	parameters in polynomial fit of $\kappa_{68}$ vs. $t_{68}$ (eqs. 7–11)
$d$	inside diameter of center tube, m
$E^\circ$	standard potential, V
$\Delta E$	averaged potential difference between two center Ag AgCl electrodes in $dc$ cell, V
$f$	frequency of sinusoidal oscillation, $\text{s}^{-1}$
$i$	current applied to $dc$ cell, A
$K$	cell constant, $\text{m}^{-1}$
$K_W$	cell constant of $ac$ cell with center extension tube, $\text{m}^{-1}$
$K_N$	cell constant of $ac$ cell without center extension tube, $\text{m}^{-1}$
$K_T$	cell constant of center tube, $\text{m}^{-1}$
$l$	length of center tube, m
$R_W$	resistance of $ac$ cell with center extension tube, $\Omega$
$R_N$	resistance of $ac$ cell without center extension tube, $\Omega$
$R_T$	resistance of solution in center extension tube, $\Omega$
$t$	celsius temperature (ITS-90), $^\circ\text{C}$
$t_{68}$	celsius temperature (IPTS-68), $^\circ\text{C}$
$U$	expanded uncertainty
$u_c$	combined uncertainty
$u_i$	component uncertainty
$x$	position along cell axis, m
$\alpha_g$	linear coefficient of expansion of glass, $\text{K}^{-1}$
$\kappa$	conductivity (ITS-90 temperature scale), $\text{S m}^{-1}$
$\kappa_{68}$	conductivity (IPTS-68 temperature scale), $\text{S m}^{-1}$

## 7. REFERENCES

1. G. Jones and B. C. Bradshaw. *J. Am. Chem. Soc.* **55**, 1780–1800 (1933).
2. H. C. Parker and E. W. Parker. *J. Am. Chem. Soc.* **46**, 312–335 (1924).
3. *Standard Solutions Reproducing the Conductivity of Electrolytes, International Recommendation No. 56, Organisation Internationale de Métrologie Légale (OIML)*, 1<sup>st</sup> ed., June 1980 (Bureau Internationale de Métrologie Légale, Paris, 1981).
4. E. Juhász and K. N. Marsh. *Pure Appl. Chem.* **53**, 1841–1845 (1981).
5. IUPAC Commission on Atomic Weights and Isotopic Abundances, *Pure Appl. Chem.* **71**, 1594–1607 (1999).

6. Y. C. Wu, K. W. Pratt, W. F. Koch. *J. Solution Chem.* **18**, 515–528 (1989).
7. Y. C. Wu, W. F. Koch, K. W. Pratt. *J. Res. Natl. Inst. Stand. Technol.* **96**, 191–201 (1991).
8. Y. C. Wu, W. F. Koch, D. Feng, L. A. Holland, E. Juhász, E. Arvay, A. Tomek. *J. Res. Natl. Inst. Stand. Technol.* **99**, 241–246 (1994).
9. Y. C. Wu and W. F. Koch. *J. Solution Chem.* **20**, 391–401 (1991).
10. G. Jones and R. C. Josephs. *J. Am. Chem. Soc.* **50**, 1049–1092 (1928).
11. *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1<sup>st</sup> ed., International Organization for Standardization, Geneva, Switzerland (1993).
12. R. A. Robinson and R. H. Stokes. *Electrolyte Solutions*, 2<sup>nd</sup> ed., pp 99–100, Butterworths, London (1959).
13. National Institute for Standards and Technology (USA), Certificate for SRM 999, Potassium Chloride, 6 September 1972.
14. P. Saulnier and J. Barthel. *J. Solution Chem.* **8**, 847–852 (1979).
15. K. N. Marsh. *J. Solution Chem.* **9**, 805–807 (1980).