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Standard Reference Materials:

Primary Standards and Standard Reference Materials for Electrolytic Conductivity

R. H. Shreiner
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Primary Standards and Standard Reference Materials for Electrolytic Conductivity

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Abstract

This report describes the principles and methods for (1) the preparation and measurement of primary and transfer standards, (2) the calibration of conductivity cells, and (3) the preparation and certification of the NIST Standard Reference Materials (SRMs). NIST has redetermined the conductivity of the “demal” primary standards and determined a set of molality-based primary standards over a temperature range of 0 °C to 50 °C. The conductivities of these primary standards were determined using two uniquely designed conductivity cells for measuring resistance with the alternating current (AC) and direct current (DC) methods. Primary and transfer standards are used to calibrate the conductivity cells. NIST issues a set of Standard Reference Materials (SRMs) available in nominal conductivity values of 5 µS/cm, 15 µS/cm, 25 µS/cm, 100 µS/cm, 500 µS/cm, 1 000 µS/cm, 10 000 µS/cm, 20 000 µS/cm, and 100 000 µS/cm. The certified conductivity values for the SRMs include the solvent conductivity.

Keywords: AC; DC; primary standards; transfer standards; conductivity; conductivity cell; electrolyte; hydrochloric acid; potassium chloride; non-aqueous solvent

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Symbols

A	effective cross-sectional area, cm^2
b	y-intercept of the curve fit of the cell calibration, Ω·µS/cm
c	specified as molality (mol/L), molarity (mol/kg), or equivalents/L
c_i	sensitivity factor
E^o	standard redox potential, V
E_{T}	potential between the potential electrodes in the DC conductance cell, V
E_{s}	potential drop across the standard resistor in DC measurement, V
ΔE	average potential difference between two center Ag, AgCl electrodes in DC cell, V
f	frequency, kHz
I	current
k	coverage factor
K_{cell}	cell constant of a conductivity cell, cm^{-1}
$K_{\mathrm{cell,\,T}}$	cell constant of the center tube of either an AC or DC absolute conductivity cell, cm^{-1}
$K_{\mathrm{cell,\,W}}$	cell constant of AC absolute conductivity cell with center tube, cm^{-1}
$K_{\mathrm{cell,\,N}}$	cell constant of AC absolute conductivity cell without center tube, cm^{-1}
l	effective length between electrodes, cm
m	slope of the curve fit of the cell calibration data, Ω
R	resistance, Ω
R_i	resistance of primary standard i, Ω
R_{initial}	initial resistance of the SRM, Ω
$R_{j,\,\mathrm{Cell\ A}}$	resistance of the transfer standard j in Cell A for the determination of κ_j (Cell A was calibrated with primary standards), Ω
$R_{j,\,\mathrm{Cell\ B}}$	resistance of the transfer standard j in Cell B when calibrating Cell B, Ω
R_{lead}	resistance of the leads (from the electrode to the binding posts of the bridge), Ω
R_{N}	resistance of a solution in the AC absolute conductivity cell without center tube, Ω
R_{s}	resistance of standard resistor used in the DC absolute measurement, Ω
R_{T}	resistance of a solution in the center tube of the DC absolute conductivity cell, Ω
R_{W}	resistance of a solution in the AC absolute conductivity cell with center tube, Ω
$R_{x\,\mathrm{kHz}}$	resistance measured at x kHz (where, typically, $x = 1$, 2, or 5), Ω
R_{∞}	resistance at infinite frequency, Ω
S	the unit for conductivity, siemens = s^3 A^2 /(m^2 kg)
t	Celsius temperature, °C
U	expanded uncertainty
$u(x_i)$	standard uncertainty
$u_{\mathrm{c}}(y)$	combined standard uncertainty
$u_i(y)$	component of the combined standard uncertainty
v_i	degrees of freedom of the component
v_{eff}	degrees of freedom of the combined standard uncertainty
Z	impedance

α_g	thermal expansion coefficient of Pyrex-type glass
α_{KCl}	temperature coefficient of aqueous KCl solutions, %/°C
κ	electrolytic conductivity of an electrolyte solution, µS·cm^{-1}
$\kappa_{certified}$	the certified electrolytic conductivity of the SRM, µS·cm^{-1}
κ_{CO2}	electrolytic conductivity of CO_2 in the solvent, µS cm^{-1}
κ_i	electrolytic conductivity of primary standard *i*, µS·cm^{-1}
κ_j	electrolytic conductivity of a transfer standard *j*, S·cm^{-1}
$\kappa_{initial}$	initial electrolytic conductivity of the SRM, µS·cm^{-1}
Λ	equivalent conductivity of an electrolyte, S·cm^{2}·equiv^{-1}
Λ^{o}	equivalent conductivity of an electrolyte at infinite dilution, S·cm^{2}·equiv^{-1}
λ	ionic equivalent conductivity, S·cm^{2}·equiv^{-1}
λ^{o}	ionic equivalent conductivity at infinite dilution, S·cm^{2}·equiv^{-1}
ρ	resistivity, Ω·cm

1. Introduction

Electrolytic conductivity is the measure of a solution's ability to conduct current. The magnitude of the conductivity is dependent on the nature of the ions (i.e., charge, size and mobility) and the nature of the solvent (such as dielectric constant and viscosity). The electrolytic conductivity is a result of ionic movement in a particular solvent, which is related to the ionic interactions taking place within the solution. The measurement of electrolytic conductivity is a nonspecific measurement; all ions contribute to the electrolytic conductivity of the solution.

In order to have uniform conductivity measurements, accurate electrolytic conductivity standards must be available for industrial use. For this purpose, the National Institute of Standards and Technology (NIST) has developed a series of electrolytic conductivity Standard Reference Materials (SRMs) and issues them through the Materals and Physical Services Group in the Measurement Services Division.

1.1 Principles of Electrolytic Conductivity

The measurement of a solution's resistance, R, in a conductivity cell, is used to determine the conductivity of a solution, κ. R is proportional to the effective length between the electrodes, l, and inversely proportional to the effective cross-sectional area, A:

$$R = \rho \frac{l}{A} \tag{1}$$

The resistivity, ρ, is a constant for a given solution. Conductivity is defined as the reciprocal of resistivity:

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\frac{l}{A} \tag{2}$$

The cell in which the conductivity is measured has a cell constant, K_{cell}, which is defined as

$$K_{\text{cell}} = \frac{l}{A} \tag{3}$$

A useful definition for the electrolytic conductivity, κ, is obtained by combining Eqs. 1-3:

$$\kappa = \frac{K_{\text{cell}}}{R} \tag{4}$$

Equations 3 and 4 assume that K_{cell} is constant for all κ. However, K_{cell} may vary with κ to a small extent owing to unknown factors [1]. Therefore, whenever possible, a conductivity cell should be calibrated over the range of κ to be determined in that cell.

Generally, a cell can be constructed in any shape; however, the cell volume and the positions of the electrodes must be rigidly fixed and, therefore, the physical dimensions of a cell, the l and A, are constant. The cell constant is determined by measuring the geometrical dimensions of the cell or by comparing with primary standard solutions in the cell. In the first case, l and A are measured directly. In the second case, the cell constant is determined from Eq. (4) with standards having a known κ. A thorough review of the measurements of and the standards for calibrating conductivity cells prior to 1987 has been discussed [2].

NIST reconfirmed the old set of standards [3,4] and established a new set of primary standards [5,6]. The new primary standards are based on the molality scale. The conductivity value for each standard has been determined at a wider range of temperatures than formerly available. Cells calibrated with these standards may be used to measure the conductivity of SRMs. In the following sections, a detailed description of these measurements will be given and discussed.

1.2 Equivalent Conductivity

Often, it is desirable to refer to equivalent conductivity, Λ, of a solution as opposed to electrolytic conductivity, κ. The equivalent conductivity is related to the quantity of ions in the solution by

$$\Lambda = \frac{1000\kappa}{c} \tag{5}$$

where c is expressed in equivalents/L. The International Union of Pure and Applied Chemistry (IUPAC) has recommended that molar conductivity be used in place of equivalent conductivity. However, the theory of electrolytic conductivity was developed in terms of equivalent conductivity, and most of the data in the early work was reported in terms of equivalent conductivity.

The equivalent conductivity, Λ, is the sum of the individual ionic conductivities, λ:

$$\Lambda = \lambda_1 + \lambda_2 + \ldots + \lambda_\mathrm{n} \tag{6}$$

Similarly, the equivalent conductivity at infinite dilution, Λ^o, is the sum of the individual ionic conductivities at infinite dilution, λ^o. Kohlrausch's Law of Independent Migration of Ions states that when ions are far enough apart that the movement of one ion is not influenced by other ions present in solution, the ions are at infinite dilution [7].

Conductivity is dependent on the quantity of the electrolyte in solution. The conductivity of a strong electrolyte generally increases with increasing amount of electrolyte due to an increase in the number of ions present.

1.3 Electrolytic Conductivity of Water

The electrolytic conductivity of a solution includes the conductivity of the solvent and solute. Hence, the conductivity of water (typically the solvent) is important.

Equation (5) and Eq. (6) can be used to calculate the theoretical electrolytic conductivity of water. For water at 25 °C, the $\mathrm{p}K_\mathrm{w} = 14$ and therefore, the amount of H^+ and OH^- ions from dissociated water molecules is $c_{\mathrm{H+}} = c_{\mathrm{OH-}} = 10^{-7}$ equivalents per liter. The $\lambda°$ for H^+ is 349.81 S cm^2 equiv^{-1} and the $\lambda°$ for OH^- is 198.3 S cm^2 equiv^{-1} [7]. The electrolytic conductivity of water is calculated by

$$\Lambda^o_{\text{water}} = \lambda^o_{H^+} + \lambda^o_{OH^-} = [198.3 + 349.81]\,\text{S cm}^2\text{equivalent}^{-1} = 549.11\ \text{S cm}^2\ \text{equivalent}^{-1}$$

$$\kappa = \frac{\Lambda c}{1000} = \frac{549 \text{ x } 10^{-7}}{1000}\,\text{S/cm} = 5.5 \text{ x } 10^{-8}\ \text{S/cm} = 0.055\ \mu\text{S/cm}$$

This theoretical value is difficult to obtain experimentally because atmospheric CO_2 is readily absorbed into water. The conductivity of water in equilibrium with atmospheric CO_2 was measured and found to be 1.05 µS/cm at 25 °C [3,4,5,6,8,9]. When other ionic contaminants are also present in water, the conductivity value will increase further. Thus, the value of conductivity is an indicator for the purity of water if this value is properly determined. To ascertain the accuracy of the measured value, low conductivity standards are needed for calibration and for quality assurance of the purity of water (see Sec. 6.3).

2. Experimental Parameters Affecting All Conductivity Measurements

The conductivity of a solution is determined by measuring the resistance of a solution in a given cell, typically using the AC method, and then calculating the conductivity from Eq. (4). The AC method uses a Wheatstone bridge or impedance meter for determining the resistance. The DC method uses a DC digital voltmeter (DVM). The details of the AC and DC methods will be described in Sec. 3. Three general issues apply to all conductivity measurements: cell cleaning, temperature control, and the CO_2 effect.

2.1 Cell Cleaning

Conductivity cells are cleaned when they are constructed, repaired, or when contamination of the cell is suspected. The cell is completely filled with chromic acid cleaning solution and soaked for 30 minutes. The cleaning solution is drained back into the bottle. The cell is rinsed with deionized water until the rinses have no yellow tinge. The cell is then completely filled with 6 mol/L HCl and soaked for 1 hour. The cell is rinsed with deionized water 5-7 times to be sure that all of the HCl is cleaned from the cell. The cell is soaked overnight with deionized water and then rinsed 5-10 times with deionized water. The cell is filled with deionized water until it is used. Strong acids and organic solvents have been tried as a replacement for chromic acid cleaning solution, without success.

2.2 Temperature Control

Electrolytic conductivity is very sensitive to changes in the temperature of the solution. The conductivity of aqueous inorganic electrolytes changes about 2 %/°C at room temperature [7]. A 0.005 °C fluctuation will cause a ± 0.01 % change in conductivity. Therefore, good temperature control is required for an accurate measurement of the conductivity of a solution.

To achieve the required temperature control, the conductivity cell is placed in a constant temperature bath that is filled with mineral oil. A temperature bath with dimensions large enough to accommodate the conductivity cells and with a temperature stability at 25.000 °C of $\leq$ 0.004 °C must be used. The homogeneity of the bath temperature is investigated by placing the thermometer in various locations and depths inside the bath and comparing the measured temperatures. The cell is positioned in the bath (as allowed by constraints of the equipment) in the location where the temperature is most stable and homogeneous.

The thermometer should have a resolution of 0.001 °C and be positioned in the bath such that it is kept stationary. At NIST, the bath temperature is monitored using a quartz thermometer connected to a frequency counter. The quartz thermometer and frequency counter are calibrated by comparison to a NIST standard platinum resistance thermometer (SPRT). When the temperature bath is correctly adjusted, the temperature can be controlled to ± 0.002 °C.

2.3 CO_2 Effect

The electrolytic conductivity of pure water equilibrated with atmospheric CO_2 is typically taken to be 1.05 µS/cm [3,4,5,6,8,9]. Carbon dioxide will dissolve and dissociate in solution producing H^+ and HCO_3^-, which will contribute to the κ of the water. The contribution of these ions to the conductivity is referred to as κ_{CO_2}. The amount of these ions is dependent on the season, latitude, altitude, atmospheric pressure, ventilation, number of people in a particular laboratory, etc. When these conditions vary, κ_{CO_2} may vary by as much as 20 %, relative (0.2 µS/cm, absolute for water). The standard uncertainty in the variation of CO_2 (0.12 µS/cm) is obtained by treating the variation of ± 0.2 µS/cm as a uniform probability distribution. The standard uncertainty of 0.12 µS/cm is applied to most aqueous solutions to account for this CO_2 effect.

Dilute HCl solutions, which have lower pH, suppress carbon dioxide dissolution and dissociation. A solution of 59 µmol/L of HCl (nominally 5 µS/cm) in equilibrium with atmospheric CO_2 is expected to have $\kappa_{CO_2} = 0.18$ µS/cm based on equilibrium conditions. The variation in κ_{CO_2} is estimated to be 20 %, relative (± 0.04 µS/cm, absolute). The standard uncertainty in the variation of CO_2 (0.023 µS/cm) is obtained by treating the variation of ± 0.04 µS/cm as a uniform probability distribution. The standard uncertainty of 0.023 µS/cm is applied to HCl solutions to account for this CO_2 effect.

In a nonaqueous-aqueous solvent, carbon dioxide dissolution and hydrogen ion conductivity is much less than that in water. Typically, the variation in κ_{CO_2} is less than ± 0.1 µS/cm [8]. The standard uncertainty in the variation of CO_2 (0.058 µS/cm) is obtained by treating the variation of ± 0.1 µS/cm as a uniform probability distribution. The standard uncertainty of 0.058 µS/cm is applied to solutions containing mixed solvents to account for this CO_2 effect.

Commercial standards and SRMs for electrolytic conductivity are prepared such that the solution is in equilibrium with atmospheric CO_2. Therefore, the user should not degas the solution prior to use. By equilibrating the solution with atmospheric carbon dioxide, the need to prepare and measure the solution in a carbon dioxide free environment is avoided.

3. General Conductivity Methods

3.1 AC Conductivity Method

The AC conductivity method has been used for the determination of the conductivity of the primary standards (Sec. 4.4) and the certification of SRMs (Sec 6). Equipment needed for these measurements and the determination of the conductivity by the AC method are described below.

3.1.1 Equipment

The AC method for conductivity measurement consists of a 2-electrode conductivity cell (discussed in Sec. 4.1.1 and Sec. 5.1.1), a constant temperature bath (previously discussed in Sec. 2.2) and the resistance measurement instrumentation.

Any equipment which measures the impedance of a solution, isolating the capacitive and resistive components, may be used to measure $R_{\mathrm{x\ kHz}}$. The resistance of a solution using an AC source may be determined either by using an oscillator, conductivity bridge, amplifier, and oscilloscope [3,6,9] or by using an impedance meter.

In previous and current NIST work [3,6,9], the $R_{\mathrm{x\ kHz}}$ of a solution has been measured using an oscillator, conductivity bridge, amplifier, and oscilloscope. The AC instrumentation [3,6,9] is described as follows. The conductivity bridge is a Jones bridge [10,11], a Wheatstone bridge with capacitance compensation, that was specifically designed for conductivity measurements. The Jones bridge is equipped with a capacitor and resistor in parallel to balance the impedance of the conductivity cell. The bridge also employs a Wagner ground to minimize the effects of stray capacitance on the accuracy of the null point. The ratio-arms are held exactly equal.

Alternating current is supplied to the bridge by a signal generator. The signal generator can be operated from 20 Hz to 15 kHz. The normal operating range of frequency, f, is 1 kHz to 5 kHz. The resistance is corrected for the effect of polarization by plotting R versus $1/f$ and extrapolating to $f = \infty$ [7]. The signal generator is modified by floating the secondary of the output transformer to obtain an ungrounded output, which is required to make use of the Wagner ground of the Jones bridge. A single-ended (unbalanced) output is obtained from a secondary winding of the output transformer and is used as the phase reference for the detector. The applied AC voltage to the bridge is 1.2 V RMS. A differential input preamplifier, tuned amplifier, and oscilloscope are used in the detector circuit. The differential input of the preamplifier preserves the balance of the Wagner ground and eliminates the need for an input transformer. The tuned amplifier is used in the bandpass mode at a Q 10 to 50 (Q is the ratio of the frequency to the bandwidth; thus, the smaller the bandwidth, the larger the Q), to attenuate the second and higher harmonics at the null point. The output of the tuned amplifier and the reference signal from the signal generator are connected to the vertical and horizontal inputs of the oscilloscope, respectively. The displayed pattern on the oscilloscope is a Lissajous figure. The Lissajous figure indicates both capacitive and resistive balance of the bridge simultaneously [12]. (This technique is superior to using the in-phase and quadrature output meters of the lock-in amplifier to indicate resistive and capacitive balance of the bridge.)

With this setup, a 0.001 % change in cell resistance may be detected on the oscilloscope. Hence, a change of 0.001 °C in the bath temperature (0.002 % in R) can be observed. The uncertainty in the null point measurement does not contribute significantly to the overall uncertainty of the measurement of the resistance of the primary standard.

3.1.2 Measurement

In the AC conductivity measurement, the cell generally has an impedance Z that is not purely resistive. However, there are other sources of impedance such as the Parker effect [1] and the effect of a conducting thermostat medium [10]. These effects can be avoided by proper cell design [1] and by using mineral oil as the thermostat medium.

When measuring the resistance of a solution, the combination of the solution conductivity and cell constant is chosen such that the measured resistance is within the optimum range of resistances for the bridge. The optimum range for resistances when using the Jones bridge is $R > 500\ \Omega$. The Jones bridge has five decade resistors plus the slide wire resistor. The standard uncertainty of the nominal readings of the dials is less than 0.01 % (for $R > 100\ \Omega$) as stated by the manufacturer.

The cell is placed into the conductivity bath for about 30 min, so that the solution in the cell can reach thermal equilibrium with the temperature of the bath. After 30 min, $R_{x\,\mathrm{kHz}}$ is measured at 2 or more frequencies (usually, $x = 1$ kHz and 2 kHz). After an additional 5 min, $R_{x\,\mathrm{kHz}}$ is measured again at the same frequencies to determine if the solution's temperature is constant. The polarization correction is made by plotting the measured resistance, $R_{x\,\mathrm{kHz}}$, vs. $1/f$ and extrapolating to $1/f = 0$ (to R_∞)[7]. If the resistance of the solution is measured at $f = 1$ kHz and $f = 2$ kHz, R may be calculated by Eq. 7, including a correction of R_∞ for R_{lead}:

$$R = R_\infty - R_{\mathrm{lead}} = 2\ R_{1\,\mathrm{kHz}} - R_{2\,\mathrm{kHz}} - R_{\mathrm{lead}} \tag{7}$$

If the resistance continuously drifts upward or downward for 30 min, this indicates that the quantity of ions in the solution is changing, or that the temperature is changing. In this instance, the measurement should be stopped, the cause of the drift determined and corrected, and the measurement repeated.

3.2 DC Conductivity Method

At NIST, the DC conductivity method [4] was used for the determination of the conductivity of the primary standards at a demality of 1.0 D and a molality of 1.0 mol/kg (Sec. 4.4). SRMs are not certified using the DC method because the AC method is more convenient. Equipment used for these measurements [4] and the determination of the conductivity by the DC method are described below.

3.2.1 Equipment

The DC method [4] for conductivity measurement consists of a 4-electrode conductivity cell (discussed in Sec. 4.2.1), a constant temperature bath (previously discussed in Sec. 2.2), a high precision digital voltmeter (DVM), an accurate standard resistor, and a constant current supply. Both the DVM and the standard resistor were calibrated by the Electricity Division at NIST. The constant current supply can provide current from 25 µA to 250 mA and has a stability of ± 0.005 % over 14 h.

3.2.2 Measurement

The wiring to the electrodes is connected according to the scheme shown in Fig. 1. The outer electrodes are connected to a constant current supply, **c**. A standard resistor, R_s, is inserted between an outer electrode and the constant current supply, so that the current passing through the cell and the R_s are the same. The inner (potential sensing) electrodes are connected to the digital voltmeter, **b**. The gaps, **A,** form the connections to the inner electrodes. Platinum wires may serve as the outer electrodes. The inner electrodes are reversible to the electrolyte solution, such as Ag|AgCl to KCl, in order to eliminate polarization.

A data point at a single current consists of four measurements as shown in Table 1. It takes approximately 3 s for each reading. Each data point is taken as the mean of three different currents. Any difference between the standard redox potentials, E°, of the potential difference-sensing electrodes is eliminated by reversing the direction of I (measurements 3 and 4 in Table 1) and averaging the magnitudes of the two measured potential differences. This averaged potential difference, ΔE, is related to conductivity by

$$\kappa = \frac{K_{\mathrm{cell,T}}}{R_{\mathrm{T}}} = \frac{I}{\Delta E} K_{\mathrm{cell,T}} \tag{8}$$

where $K_{\mathrm{cell,T}}$ is the cell constant of the center tube (Sec. 4.2.1), and R_{T} is the resistance of the solution in the tube.

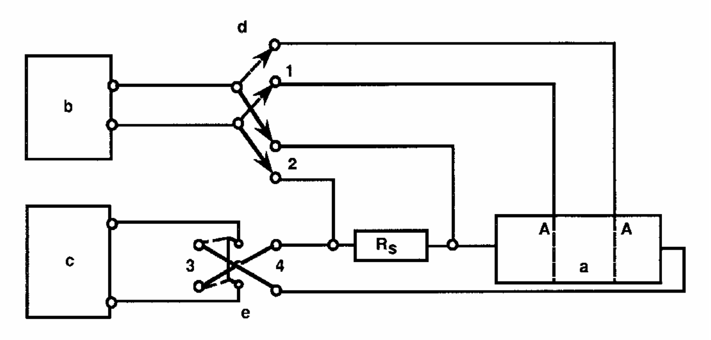

Figure 1. Schematic of DC Operating and Switching Circuitry: a – conductivity cell with gaps A; b – digital voltmeter; c – constant current supply; d – switch with position 1 and 2; e – switch with position 3 and 4; R_{s} – standard resistor

Table 1. Measurement Sequence[4]

Measurement Number	Switch d	Switch e	Results
1	2	3	I flows through R_{s} and the cell; E_{s} is measured ($E_{\mathrm{s}} = IR_{\mathrm{s}}$); I is calculated.
2	1	3	E_{T} is measured ($E_{\mathrm{T}} = IR_{\mathrm{T}}$); R_{T} is calculated
3	1	4	reverses flow of I and the polarity of the electrodes
4	2	4	reverses flow of I and the polarity of the electrodes

3.3 AC vs. DC

For measurement of conductivity, there are limitations of dimension for the constant temperature bath and for the conductivity cell. Hence, the range of cell constants is limited. Thus, the AC method is preferred for solutions of low conductivity and high resistance due to lower experimental uncertainties. The DC method is preferred for solutions of high conductivity, and hence low resistance. For the AC method, an optimum range of resistance is required for the best accuracy. Typically, an error in the resistance of a few hundredths of an ohm would result from either the bridge or the lead resistance. For example, if R is 100 Ω, an error of 0.05 Ω absolute is equivalent to an error of 0.05 % relative. If R is 1000 Ω, an error of 0.05 Ω absolute is equivalent to an error 0.005 % relative. Therefore, a larger cell constant, which is difficult to achieve, is necessary when using the AC method to minimize these effects. When the DC method is used, errors due to the bridge and the lead resistance are eliminated. Because the potential measured (ΔE) does not include the leads, the lead resistance is eliminated. The accuracy of a voltmeter can reach 10^{-7} V to 10^{-8} V. An applied current may be selected from 10^{-5} A to 10^{-2} A. For a given cell constant, κ can be varied a thousandfold and can be determined without sacrificing accuracy.

4. Absolute Conductivity Measurements

Absolute conductivity measurements used at NIST were performed using conductivity cells, the cell constants of which were determined by electrical and physical standards. Both the AC and DC methods, described in the following sections, have been used to measure the conductivity of the primary standards. The work performed in this laboratory [3,4,5,8,9], and described in this report, has taken several years. The data are listed in Tables 2-4.

The two absolute methods, AC and DC, use different instrumentation (described in Sec. 3) and conductivity cells. The absolute conductivity measurement was used at NIST to redetermine the conductivity of the OIML primary standards [3,4,13] (see Table 2 and Sec. 4.4.1) and to establish the molality-based "NIST" primary standards [4,5,6]. These primary standards may then be used to calibrate other types of cells (Sec. 5).

Table 2. Definition of Demal (D) for 0.01D, 0.1D, and 1.0 D KCl Solutions[13]

Demality	grams of KCl per kilogram of solution
0.01	0.745 263
0.1	7.419 13
1.0	71.135 2

Table 3. Electrolytic Conductivity Values for 0.01D, 0.1D, and 1.0 D KCl Solutions[a] and Water, ITS-90 Scale

t/°C	κ/(μS/cm)[b]			
	0.01 D KCl[3]	0.1 D KCl [3]	1.0 D KCl [4]	H_2O[3,4]
0	773.09	7 134.6	65 135	0.58
5	891.20	8 200.0	73 860	0.68
10	1 014.2	9 308.7	82 871	0.79
15	1 141.8	10 457	92 136	0.89
18	1 220.3	11 162	97 804	0.95
20	1 273.4	11 639	101 620	0.99
25	1 408.6	12 852	111 300	1.10
30	1 547.0	14 091	121 110	1.20
35	1 688.2	15 352	131 050	1.30
40	1 831.8	16 631	141 080	1.40
45	1 977.3	17 922	151 150	1.51
50	2 124.2	19 222	161 240	1.61

[a] Values of conductivity for KCl solutions do not include solvent conductivity
[b] The standard uncertainty is taken as 0.03 % to 0.04 % (Sec. 4.4.1)

Table 4. Electrolytic Conductivity Values for the Molality-Based Primary Standard KCl Solutions[a] 0.01 mol/kg, 0.1 mol/kg, and 1.0 mol/kg, ITS-90 Scale[5]

t/°C	$10^4\,\kappa$ / (μS/cm)						
	0.01 mol/kg		0.1 mol/kg		1.0 mol/kg		water
	value	$2u_c$	value	$2u_c$	value	$2u_c$	value
0	772.92	0.23	7 116.85	2.85	63 488	25	0.58
5	890.96	0.27	8 183.70	3.27	72 030	29	0.68
10	1 013.95	0.30	9 291.72	3.72	80 844	32	0.79
15	1 141.45	0.34	10 437.1	4.2	89 900	36	0.89
18	1 219.93	0.37	11 140.6	4.5	---	---	0.95
20	1 273.03	0.38	11 615.9	4.6	99 170	40	0.99
25	1 408.23	0.42	12 824.6	5.1	108 620	43	1.10
30	1 546.63	0.46	14 059.2	5.6	118 240	47	1.20
35	1 687.79	0.51	15 316.0	6.1	127 970	51	1.30
40	1 831.27	0.55	16 591.0	6.6	137 810	55	1.40
45	1 976.62	0.59	17 880.6	7.2	147 720	59	1.51
50	2 123.43	0.64	19 180.9	7.7	157 670	63	1.61

[a] Values of conductivity for KCl solutions do not include solvent conductivity

4.1 AC Absolute Method

The AC absolute cell was designed and constructed at NIST for the measurement of the OIML primary standards at 0.01 D and 0.1 D (see Sec. 4.4.1 for more on the unit demal) [3,13] and the NIST molality-based primary standards at 0.01 mol/kg and 0.1 mol/kg [5,6] (Sec. 4.4.2). This AC absolute cell and its design are described in the following sections.

4.1.1 Cell Design

The AC absolute cell (Fig. 2) is a Jones type cell with a removable center tube. The design of this cell allowed determination of the conductivity of a solution from basic standards. No calibration of the cell is necessary.

The details of cell construction [3,6,9] are briefly described as follows. A length of precision-bore Pyrex tubing having an inner diameter (ID) of 1 cm, with uniformity certified by the manufacturer, was cut into 3 sections. A prefabricated flange, **c**, with an ID of 1.3 cm, outer diameter (OD) of 2.5 cm, and thickness of 0.65 cm was epoxied into each of the tubes such that the face of the flange was flush with the cut end of the tube. Each flanged end was ground to optical flatness. The unflanged end of each of the singly flanged tubes was joined to the corresponding electrode chamber, **a**, each of which contained a 2 cm platinum disk electrode, **d**. The electrodes were gold soldered to a 2 mm platinum wire, which extended through a graded-glass seal (see Sec. 5.1.2 for a detailed discussion on graded seals). To assemble the cell, the mating flange ends were held together by a C-shaped Bakelite band which can be slightly enlarged with a little pressure, such that the two flanges fit snugly into it, preventing the flanges from moving laterally.

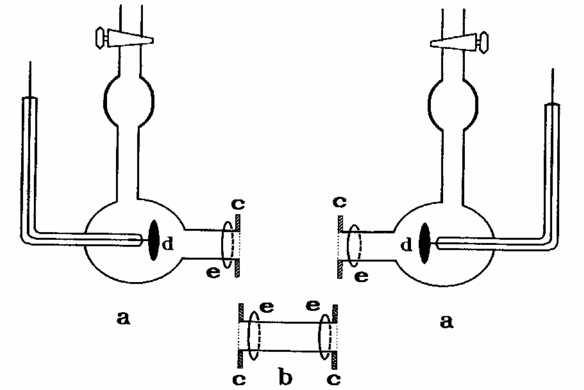

Figure 2. AC absolute conductivity cell: a – electrode chambers (half-cells); b – removable center tube; c – flanges; d – platinum disk electrodes; e – O-rings. The mating flange ends are held together by a C-shaped Bakelite band (not shown) so that lateral movement is prevented.

Lateral and rotational movements were prevented by a Bakelite two-plate assembly tightened together with four nylon screws and nuts. A rubber O-ring, **e**, was inserted between each plate and the rear side of the flange. The tube **b** of the cell was removable, and its dimensions (length and internal diameter) were determined by the Length and Mass Division of NIST (presently, length is determined by the Precision Engineering Division).

Since the cell constant in a Jones-type conductance cell is determined by the lines of force between the two electrodes, the center section of the tube may be removed in order to shorten the distance between the electrodes, thereby reducing the resistance. Subsequently, the same section may be put back, lengthening the distance and increasing the resistance, provided that the lines of force are not disturbed. Thus, there were essentially two cells: one was with the center tube **b**, and the other was without the center tube **b**. When κ was measured with the two cells, the resistance of the solution in the cell with the center tube, R_W, was

$$R_\mathrm{w} = \frac{K_\mathrm{cell,w}}{\kappa} \tag{9}$$

and the resistance of the solution in the cell without the center tube, R_N, was

$$R_\mathrm{N} = \frac{K_\mathrm{cell,N}}{\kappa} \tag{10}$$

where $K_\mathrm{cell,\,W}$ and $K_\mathrm{cell,\,N}$ are the cell constants with and without the center tube, respectively. Similarly, R_W and R_N are measured resistances when using the cell with the center tube and without the center tube, respectively.

Equation (9) and Eq. (10) may be combined by subtracting R_N from R_W and solving for κ:

$$\kappa = \frac{K_\mathrm{cell,\,W} - K_\mathrm{cell,\,N}}{R_\mathrm{W} - R_\mathrm{N}} = \frac{K_\mathrm{cell,\,T}}{R_\mathrm{W} - R_\mathrm{N}} \tag{11}$$

The cell constant of the center tube, $K_\mathrm{cell,\,T} = l/A$, was determined by physical measurements of l and A and is equal to $K_\mathrm{cell,\,W} - K_\mathrm{cell,\,N}$. All the quantities on the right-hand side of Eq. (11) were known by means of physical measurement. Therefore κ was absolutely determined and values for $K_\mathrm{cell,\,W}$ and $K_\mathrm{cell,\,N}$ were calculated from Eq. (9) and Eq. (10).

4.1.2 Preparation of the AC Absolute Cell for Measurement

After the cell was thoroughly cleaned (see Sec. 2.1) and dried, it was assembled and filled with a standard KCl solution. If no leak was detected at the joints after the filled cell stands for 1 h, the cell was put into the bath for 30 min to 40 min until the solution reaches thermal equilibrium with the bath temperature. The reading was then recorded. If no drift was noted over a 1 h period, the cell was emptied and refilled to obtain measurements in triplicate. If the deviation of the results was less than 0.01 % and random, the mean was taken as the final result. If the deviation showed a trend toward increasing or decreasing resistance, there were two probable causes: evaporation of water from the solution (decreasing trend) and/or cell contamination (increasing or decreasing trend). If the trend is toward decreasing resistance, the experiment should be repeated to determine if the cause is evaporation of water in the solution. If the trend toward decreasing resistance continues, then the cause is cell contamination. Cell contamination is generally caused by adsorption of foreign substances on the cell walls and/or electrodes. The experiment may be repeated until the foreign substances are leached out or the cell must be cleaned (Sec. 2.1). If the experiment is repeated with reasonable effort and the readings do not stabilize, the cell must be cleaned (Sec. 2.1).

The procedures for changing between solutions of different ionic contents and/or for replacing the center tube of the cell were similar. The cell was taken out from the bath, the outside wall of the cell and the whole assembly was washed with soap solution and rinsed with water. The inside of the cell was flushed with distilled water continuously for about 30 min. The whole unit was dried with paper towels and was disassembled. The joints of the cell were cleaned with soap and water. When everything was dry, they were re-assembled. Caution was always exercised to prevent the oil on the outside of the cell from creeping inside. If oil crept inside the cell, the cleaning process was repeated.

4.2 DC Absolute Method

At NIST, the DC absolute cell was designed for the measurement of the OIML primary standard at 1 D (see Sec. 4.4.1 for more on the unit demal) [4,13] and the NIST molality-based primary standard at 1 mol/kg (Sec. 4.4.2) [4,5]. The DC absolute cell and its design are described in the following sections.

4.2.1 Cell Design

The DC absolute cell was a four-electrode conductivity cell (Fig. 3): 2 potential-sensing (inner) electrodes and 2 current-sensing (outer) electrodes. The preparation and calibration of these electrodes have been described in conjunction with the pH studies at NIST [14]. All four electrodes were within ± 0.05 mV of each other. Reversible electrodes were required to eliminate polarization effects. Ag, AgCl electrodes, appropriate for KCl solutions, were used for all four electrodes to minimize the effects of electrolysis and polarization.

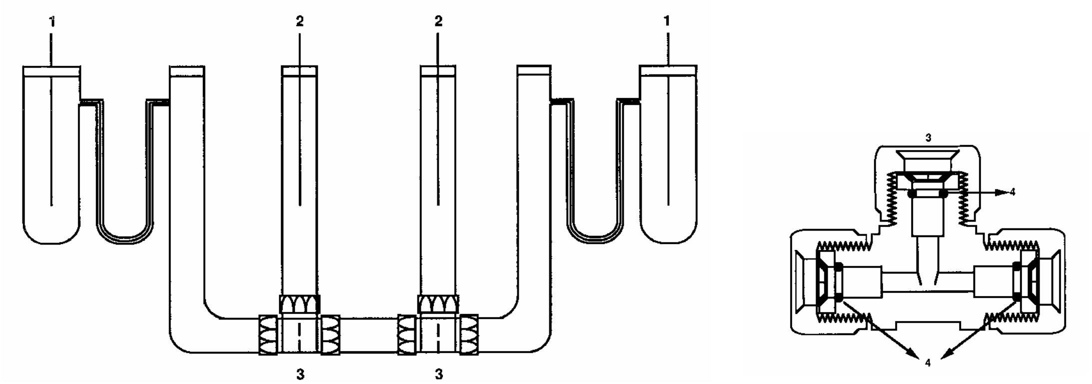

Figure 3. DC Absolute conductivity cell: 1 – current electrodes; 2 – potential difference sensing electrodes; 3 – nylon tee joints; 4 – O-rings.

For an absolute determination of conductivity, the cell constant needed to be determined with the same basic standards (e.g., length measurement) as the AC cell. To accomplish this requirement, a precision bore Pyrex tubing was cut into three pieces, so that the center section of the cell could be removed and that the internal diameter and length of this center section could be measured accurately by physical methods. The two ends of the center section were polished to flatness, while the surfaces of the ends of the other two pieces, which joined with the center section, were ground to a roughness of about 25 µm. A slight gap was formed between the joined ends of the tubing to effect a miniscule flow of solution, when the sections were rejoined using a nylon union. The other two ends of the cut tubing were fused to Pyrex tubing comprising the current compartments of the cell. A U-shaped capillary separated the current-electrode chamber from the connecting chamber to minimize the effect of electrolysis products on the measurement. A third tube was joined at each of the junctions of the center section with the end sections using a nylon-union tee. These compartments contained the potential leads for the measurements. The final assembly is shown schematically in Figure 3.

4.2.2 Preparation of the DC Absolute Cell for Measurement

The cell is cleaned when it is newly constructed (see Sec. 2.1). The procedure used for changing between solution of different ionic content is the same as described in Sec. 4.1.2 . After the cell was assembled and filled with solution, the electrodes were placed in the appropriate chambers. The whole cell assembly was put into the bath, and the temperature was adjusted and controlled as designated.

4.3 Temperature Effect on the Center Tube

For an absolute conductivity cell, where the center tube is removable, the effect of temperature, *t*, on the cell constant of the center tube is given by [7]:

$$\left(\frac{\partial K_{\text{cell}}}{\partial t}\right)\frac{1}{K_{\text{cell}}} \approx \left(\frac{\partial l}{\partial t}\right)\frac{1}{l} - \left(\frac{\partial A}{\partial t}\right)\frac{1}{A} = \alpha_{\text{g}} - 2\alpha_{\text{g}} = -\alpha \tag{12}$$

where $\alpha_g = 3.6 \times 10^{-6}$ °C^{-1}, the thermal expansion coefficient of the Pyrex-type glass used to construct the tube. For the whole range of temperatures, 0 °C to 50 °C, the change in K_{cell} is approximately 0.02 %.

4.4 Primary Standards

Establishment of conductivity values for primary standard solutions requires the use of the absolute method and is the primary purpose of the absolute method. The chief requirement for the standard is accuracy. The factors affecting the accuracy of the primary standards include stability of the chemical, purity of the solute and solvent, and ionic content of the solution. Potassium chloride was chosen as the solute because KCl is stable and easily purified. Water is used as the solvent because it is stable, easily purified, and the most practical choice. These two factors are very important for maintaining uniformity and repeatability when the solutions are prepared in different laboratories, so that the results can be accurately compared. For high accuracy measurements, the molality (or demality) of the primary standard solutions should be accurate to at least 5 places.

Primary standards are used for calibrating conductivity cells. The conductivities of the primary standards were determined using absolute measurements. There are two types of primary standards: (1) those recommended by the Organisation Internationale de Métrologie Légale (OIML) [13] and (2) those determined by NIST [3,4,5,6] and adopted by the International Union of Pure and Applied Chemistry (IUPAC) [5].

4.4.1 OIML Primary Standards

Currently, three primary standards at three temperatures are recommended by OIML [14]. These primary standards are based on the measurements of Jones and Bradshaw [15]. The primary standards have ionic contents defined by the so-called demal (D) scale. A demal is defined as an exact mass of KCl in an exact mass of water. This scale is not directly related to other scales of concentration (i.e., molality, molarity). The demal unit is defined at three levels only (Table 2): 0.01 D, 0.1 D, and 1.0 D.

The measurements of the primary standards by Jones and Bradshaw [15] were performed over 60 years ago and several SI units have been redefined (see Sec. 5.2.1.4). The demal scale lacks a direct relationship to the common units of concentration and to the units used in solution chemistry. In addition, the conductivities of the recommended demal standards are only defined at three temperatures (0 °C, 15 °C, and 25 °C).

NIST developed two absolute conductivity methods (Secs. 4.1 and 4.2). Using the absolute methods, NIST redetermined the conductivity values for the OIML primary standards over a wider temperature range (Table 3) [3,4]. The conductivities determined at NIST agreed to ± 0.02 % with the values of Jones and Bradshaw [15]. The uncertainties of the NIST determined values is estimated to be 0.03 % to 0.04 % [3,4]. No uncertainties were stated for the original values of Jones and Bradshaw [15].

4.4.2 NIST Molality-Based Primary Standards

NIST also used the absolute conductivity methods (Secs. 4.1 and 4.2) to determine a set of molality-based primary standards (NIST primary standards). The NIST primary standards were determined at temperatures from 0 °C to 50 °C at 5 °C intervals, and at 18 °C (Table 4) to expand the applicability of primary standards [4,5,6]. The NIST primary standards were prepared using potassium chloride and water. Molality, mol/kg, is defined as the amount of solute in one kilogram of solvent *in vacuo*. The NIST primary standards expressed in molality (0.01 mol/kg, 0.1 mol/kg, and 1.0 mol/kg) in the temperature range of 0 °C to 50 °C have been adopted by IUPAC [5].

The values for the conductivity of the NIST primary standards (Table 4) were calculated using Eq. 13, which is a polynomial fit of the values for conductivity at each temperature:

$$\kappa / \kappa^{\mathrm{o}} = a + b\left(\frac{t}{t^{\mathrm{o}}}\right) + c\left(\frac{t}{t^{\mathrm{o}}}\right)^2 + d\left(\frac{t}{t^{\mathrm{o}}}\right)^3 \qquad (13)$$

where t^{o} = 1 °C is a standard temperature, and κ^{o} = 1 S/m is a standard conductivity. The values for a, b, c, and d are given in Table 5.

Table 5. Parameters in the Polynomial Fit for Electrolytic Conductivity Versus Temperature[5]

Molality, mol/kg	Parameters			
	a	***b***	***c***	***d***
0.01	0.077 2921	$2.308\ 46 \times 10^{-3}$	$1.077\ 15 \times 10^{-5}$	$-5.840\ 94 \times 10^{-8}$
0.1	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	$1.679\ 13 \times 10^{-1}$	$6.007\ 81 \times 10^{-4}$	$-3.837\ 02 \times 10^{-6}$

4.4.2.1 Uncertainty Analysis for the NIST Primary Standards

The values of c_i, $u(x_i)$, $u_i(y)$, $u_c(y)$, k, and U are calculated following the ISO guidelines [16]. The values of $u_i(y)$ are combined using propagation of uncertainty to obtain $u_c(y)$. The $u_c(y)$ was multiplied by 2 to obtain a U at the 95 % confidence interval [16].

The uncertainty analysis [5] for the conductivity measurements of the molality-based primary standards using the AC and DC contained several errors, which have been corrected in this document. The values of $u_i(y)/y$ (i.e., the "relative" $u_i(y)$) are given in Table 6. The value of c_i for each component uncertainty is 1. Therefore, $u(x_i)/x_i = u_i(y)/y$.

Table 6. Uncertainty Determination for the NIST Primary Standards

Component x_i	$u_i(y)/y$ for each molality-based primary standard/%		
	1409.33 µS/cm	12 825.7 µS/cm	108 621 µS/cm
Difference between the smoothed and discreet κ values[a]	0.004 6	0.013	0.015
Measurements of length and diameter for $K_{\mathrm{cell,\,T}}$[a]	0.006 5	0.006 5	0.008 5
Temperature effect on $K_{\mathrm{cell,\,T}}$ calculated from Eq. (12)[a, b]	---	---	0.005 2
Thermometer calibration[c]	0.008 6	0.008 5	0.003 0
Impurities in the KCl[a]	0.002 5	0.002 5	0.002 5
Evaporation of the solution during transfer to the cell[d]	0.002 9	0.002 9	0.002 9
Electrical measurements	0.000 58[d]	0.000 58[d]	0.000 61[a]
Conductivity of the solvent from atmospheric CO_2[e]	0.008 2	0.000 90	0.000 11
$u_c(y)$	0.015	0.017	0.018
U ($k = 2$)	0.030	0.034	0.037
Actual values of U based on a conservative estimate[a]	0.03	0.04	0.04

[a] ref. [5]

[b] AC measurements: $K_{\mathrm{cell,\,T}}$ was corrected for changes in t; $u_i(y)$ for the correction was insignificant. DC measurements: no correction was applied to $K_{\mathrm{cell,\,T}}$; $u_i(y)$ is based on the estimated change in $K_{\mathrm{cell,\,T}}$ with t.

[c] α was always highest at 0 °C: 2.99 %/°C for $\kappa = 1409.33$ µS/cm, 2.94 %/°C for $\kappa = 12\ 825.7$ µS/cm, and 2.63 %/°C for $\kappa = 108\ 621$ µS/cm. For AC measurements, the largest $u_c(t) = 0.0029$ °C (uniform probability distribution) for the thermometer calibration was at 0 °C. For DC measurements, $u_c(t) = 0.0012$ °C (uniform probability distribution) at all temperatures (0 °C to 50 °C). $u_i(y)/y = \alpha \cdot u_c(t)$.

[d] treated as a uniform probability and divided by the square root of 3 [16].

[e] The conductivity of the solvent may vary by as much as 0.2 µS/cm; $u_i(y) = 0.12$ µS/cm (uniform probability distribution).

5. AC Conductivity Measurement With Other Cells

As mentioned in Sec. 4.4, the primary standards are used to calibrate conductivity cells. Absolute cells are used when the best possible accuracy is needed. Some solutions, such as SRMs, do not require the high accuracy measurement that primary standards require. For SRMs, fixed-geometry cells, Jones and Daggett cells [7], are used for making the resistance measurements. The Jones and Daggett cells are calibrated with primary standards and/or transfer standards. Primary standards are described in Sec. 5.2.1.1. Transfer standards are described in Sec. 5.2.1.2.

5.1 Cell Design and Fabrication

5.1.1 Design

Jones cells are composed of two glass bulbs, each containing a platinum disk electrode, separated by a piece of glass tubing to give a large cell constant (Fig. 4). To minimize evaporation when filling the cell, the solution is poured through a funnel and into the cell. Less evaporation occurred with this type of filling than with the other methods examined in this laboratory. Significant evaporation of the solution will change the conductivity of the solution and will lead to an inaccurately calibrated cell.

Daggett cells consist of an Erlenmeyer flask that is connected to a glass bulb containing the electrodes (Fig. 5). The use of the Erlenmeyer flask facilitates filling of the cell. However, an Erlenmeyer flask can only be attached to cells with small cell constants due to design problems. Daggett cells are typically used for low conductivity solutions.

The conductivity cells are designed such that the cell constant, K_{cell}, when determined based on the distance between the electrodes and the cross-sectional area of the electrodes, has the desired value. However, l and A are the effective length and effective cross sectional area, respectively. The "true" value of K_{cell} must be determined via the cell calibration.

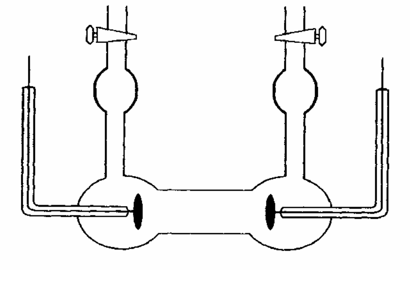

Figure 4. Jones Cell: Jones cell is similar to the AC absolute cell except that it does not have a removable center tube.

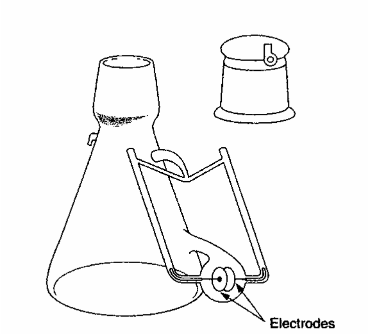

Figure 5. Daggett cell: diagram is similar to the Jones cell, except that an Erlenmeyer flask is attached to facilitate filling of the cell.

5.1.2 Fabrication

All of the Jones and Daggett cells used at NIST were made on-site. The cell body is made out of borosilicate (Pyrex®) glass. A scientific glassblower of high skill level would be able to duplicate the cell body and electrodes for any type of conductivity cell.

The conductivity cells must not contain rough edges or ridges. Any micro cracks where the solute could be trapped must be eliminated. When adding a solution to the cell, any trapped solute would diffuse into the solution. The quantity of ions in the solution, and therefore the conductivity, would change. Two types of micro cracks have been observed with commercial cells: (1) at the joining of the platinum rod to the platinum disk and (2) at the joining of the platinum to the glass.

The platinum disc electrode is punched out of a platinum sheet to obtain a clean edge with no burrs. The center of the platinum disc is spot welded to the platinum rod and this connection is braised with pure gold to avoid microcracks.

The glass used to form a hermetic seal to the platinum rod must wet the platinum. The "platinum seal" is made using a soft glass that contains no Pb and and wets the platinum rod without forming micro cracks. (Pyrex-type glasses do not wet the platinum, causing the glass to pull away from the rod leaving small cracks where KCl could be trapped). A graded seal of 5 glasses is required to seal the soft glass used for the "platinum seal" to the Pyrex-type glass used for the cell body. The glasses must be assembled in order of their coefficient of thermal expansion (C.O.E.).

The platinum post is welded to thinner Pt wires, which run up to the next graded seal at the mercury well. This graded seal consists of tungsten sealed to uranium glass, that is then graded to the Pyrex-type glass of the cell body. This graded seal will hold the mercury and prevent leaks. The tip of the tungsten must have a drop of platinum welded to the end so that the mercury can wet the electrode.

The graded seals are then sealed to the side arms of the cell. The side arm is evacuated after all seals are completed.

The resistance from the platinum disk to the tip of the tungsten is measured using a digital voltmeter. This resistance, along with the resistance of the connection from the cell to the bridge, is referred to as the lead resistance (see Eq. 7).

The side arms (graded seals, electrode, platinum wire, etc.) are attached to the cell body.

5.2 Calibration of Cells

The calibration of conductivity cells involves the preparation and measurement of several standards.

Primary standards or transfer standards are used for calibrating a cell. Generally, on each of 3 days, several standards at each conductivity are separately prepared (in random order) and measured (in a different random order). After all of the measurements have been made, the data is examined for day-to-day differences, within day differences, and measurement trends.

5.2.1 Choosing Standards for Calibrating the Cell

Primary standards [3,4,5,6,13] or transfer standards may be used to calibrate the cell. Primary standards are the preferred standards when R_i is in the allowed range for a given cell. If the measured resistance is less than 500 Ω, the accuracy of the resistance measurement would be compromised because the lead resistance and its uncertainty become significant.

The standards should be chosen such that the smallest possible uncertainty for the cell calibration can be obtained. A cell should be calibrated at 1 to 3 different levels of conductivity while taking into account the $u(R_{\mathrm{x\ kHz}})$ and the significance of R_{lead} (R_{lead} should be insignificant when compared to $R_{\mathrm{x\ kHz}}$).

The cells must not be calibrated with the OIML secondary standards [13] or secondary standards prepared the Onsager Limiting Law [2,17]. The accuracy of these secondary standards has not been verified. The OIML secondary standards were determined by Shedlovsky [19], using the original Jones and Bradshaw standards [15] to calibrate his cell. The uncertainties of the OIML secondary standards [13] are not stated. The Onsager limiting law equation [2,17] for KCl as a function of molarity has been used by some workers in this field to prepare secondary standards of the of low molality (< 0.05 mole/L). However, the limiting law equation does not account for the solvent conductivity and the uncertainties of these secondary standards is not stated.

5.2.1.1 Primary Standards for Cell Calibration

NIST-traceable primary standards can be prepared accurately, with a relative combined standard uncertainty of about 0.02 %, using any issue of SRM 999 (KCl) and water (> 16 MΩ·cm water) [18]. The primary standards are prepared to within ± 0.005 % of the target molality. The combined standard uncertainty in the molality includes the uncertainty components for the masses of KCl and water, the buoyancy corrections for KCl and water, the purity of the KCl, the molecular weight of KCl, and the literature value of the conductivity. The detailed preparation instructions and uncertainty determination have been discussed in detail [18]. The resistance of the primary standard, R_i, is determined in the cell to be calibrated.

5.2.1.2 Transfer Standards for Cell Calibration

Transfer standards are prepared as needed in the laboratory to approximate molalities. Accurate knowledge of the molalities of these solutions is not necessary. Generally, on each of 3 days, 5 standards are prepared (in random order) and measured (in a different random order). On each day, the solutions have nominally the same conductivity.

The conductivity of the standard is determined by determining the resistance of the solution, $R_{j,\,\mathrm{Cell\ A}}$, in a cell calibrated with primary standards, Cell A. The conductivity, κ_j, is calculated as described in Sec. 3.1 using the results of the calibration of Cell A. The resistance, $R_{j,\,\mathrm{Cell\ B}}$, of the transfer standard is then measured in the cell to be calibrated, Cell B. The values of $R_{j,\,\mathrm{Cell\ B}}$ and κ_j are used for modeling the data for Cell B. No replicate measurements are performed when using transfer standards.

The determination of $R_{j,\,\mathrm{Cell\ A}}$ and $R_{j,\,\mathrm{Cell\ B}}$ MUST be performed consecutively, but either may be measured first. This protocol minimizes changes in κ_j owing to evaporation of the transfer standard for the two measurements.

The uncertainty in the conductivity of these transfer standards is calculated from the determination of κ_j. The uncertainty components that must be considered are temperature, $R_{j,\,\mathrm{Cell\ A}}$, the CO_2 effect, and the conductivities and resistances of the calibrants used to calibrate Cell A.

5.2.2 Measurements for Cell Calibration

The cells are calibrated at the same temperature (usually, $t = 25.000\ °C \pm 0.004\ °C$) at which the SRMs are certified. Each standard is measured once in the cell. The measurement of resistance and calculation of the resistance of the solution are discussed in Sec. 3.1.

5.2.3 Analysis of the Calibration Data

Typically, the data (κ_i and R_i and/or κ_j and $R_{j,\,\mathrm{Cell\ B}}$) is fit to a linear model with either all of the points on one straight line or with pairs of points forming several straight lines. Usually, the curve is of the form $\kappa_i R_i$ vs. κ_i (or $\kappa_j R_{j,\,\mathrm{Cell\ B}}$ vs. κ_j). The choice of model is dependent on the data and must be examined for each calibration. Each straight line is of the form:

$$\begin{aligned} \kappa R &= m\kappa + b \\ \kappa &= b/(R - m) \end{aligned} \tag{14}$$

where m and b are determined by regression analysis or another appropriate statistical analysis, and R and κ refer to the SRM.

In the trivial cases, where the cell is calibrated at only one conductivity, or where $m = 0$, Eq. (15) becomes

$$\kappa = \frac{b}{R} \tag{15}$$

As in Eq. (4), $b = K_{\mathrm{cell}}$.

6. Standard Reference Materials (SRMs)

To satisfy industrial needs, NIST certifies and issues a series of electrolytic conductivity SRMs (Table 8). The conductivity of these standards includes the solvent conductivity.

All but two of the aqueous SRMs are prepared as KCl in water. The solute for the 25 µS/cm solution is hydrochloric acid. Hydrochloric acid is used for lower conductivity solutions because it suppresses carbon dioxide dissociation at its low pH (Sec. 2.3). The solute for the 20 000 µS/cm solution is NaCl. The use of NaCl was specifically requested by clinical laboratories. When the

20 000 µS/cm solution is made with NaCl, the ionic strength of the solution approximates the ionic strength and composition of body fluid.

The two lowest conductivity SRMs are prepared using KCl in 30 % n-propanol 70 % water. These SRMs are discussed further in Sec. 6.3.

Table 7. Summary Information for the SRMs

SRM	Nominal Conductivity/(µS cm^{-1})	SRM Composition	% maximum acceptable 3 h drift (bulk solution)
3190	25	HCl in water	0.07
3191	100	KCl in water	0.03
3192	500	KCl in water	0.03
3193	1 000	KCl in water	0.03
3194[a]	10 000	KCl in water	0.03
3195[a]	100 000	KCl in water	0.03
3196[a]	20 000	NaCl in water	0.03
3198	5	KCl in 30 % n-propanol 70 % water	0.5
3199	15	KCl in 30 % n-propanol 70 % water	0.5

[a] These SRMs may be discontinued. Customers interested in these SRMs could prepare their own standard following the guidelines given in [18].

6.1 Preparation and Measurement of SRMs

The SRMs are prepared by underestimating the amount of solute needed for a given amount of solvent that will give the desired conductivity. Since the SRMs are certified based on conductivity, the exact mass fraction of KCl is not critical. Any minor contamination of the bulk solution (prior to certification) will not spoil the SRM. The bulk solution is shaken for several days to ensure that the solution is homogenous and to ensure that the solution has equilibrated with atmospheric CO_2. Using the AC method (Sec. 3.1) and a calibrated Jones or Daggett cell (Sec. 5.2), the resistance of a sample of the bulk solution is measured over 3 h. If the drift in the conductivity of the bulk solution is acceptable (Table 8), the solution has equilibrated with atmospheric CO_2. The mass fraction of KCl in the solution may be adjusted by adding solute or solvent to get closer to the nominal conductivity.

The solution is packaged, typically yielding 20 to 80 units of the SRM. A stratified random sampling, based on the packaging order, is used to determine which units will be measured. The measurements of these units are randomized so that trends in bottling order and measurement order may be differentiated. The mean resistance, R_{initial}, from the randomly selected units is used to calculate the initial mean value, $\kappa_{\mathrm{initial}}$.

6.2. Value Assignment and Uncertainty Analysis for SRMs

The certified value, $\kappa_{\mathrm{certified}}$, of an SRM may include an adjustment for instability (leaching, evaporation, or transpiration). The expected change in the $\kappa_{\mathrm{initial}}$ over the certified period is estimated. Typically, the value of $\kappa_{\mathrm{certified}}$ is calculated by taking half of the estimated change and adding it to $\kappa_{\mathrm{initial}}$.

The expanded uncertainty of the SRM is evaluated following the mandated ISO procedures

[16]. The expanded uncertainty is determined at the 95 % confidence level. The components to the uncertainty for an SRM measured in a cell that was calibrated transfer standards are listed in Table 9.

For an SRM measured in a cell that was calibrated with primary standards, components that refer to tranfer standards are irrelevant. Additional uncertainty components are included as needed.

Table 8. Uncertainty components for the determination of the certified value of a SRM[a]

Standard Type	Component x_i	Source of $u(x_i)$
Transfer Standards	κ_j from the uncertainty in the determined value, including CO_2	see Sec. 5.2.1.3
	$R_{j,\,\mathrm{Cell\ B}}$ from the equipment specifications and/or calibration	Manual/Calibration report
	t from the variation observed when measuring solutions having κ_j	Observed[c]
Primary Standards	κ_i from the uncertainty in the literature value, including CO_2	see Tables 3, 4, and 6
	κ_i from the molality of the solution	calculated [18]
	R_i from measurement replication	Observed[b]
	R_i from the equipment specifications and/or calibration	Manual/Calibration report
	t from the variation observed when measuring solutions having κ_i	Observed[c]
SRM	$\kappa_{\mathrm{certified}}$ from CO_2 fluctuations in users' laboratories	0.12 µS/cm (Sec. 2.3)
	$\kappa_{\mathrm{certified}}$ from instability	Calculated
	R_{initial} from measurement replication	Observed[b]
	R_{initial} from the equipment specifications and/or calibration	Manual/Calibration report
	t from the thermometer calibration	Calibration report
	t from the variation observed when measuring the SRM	Observed[c]

[a] if the cell used for the measurement of the SRM was calibrated with primary standards standards, those of listed uncertainty components related to tranfer standards should be ignored.
[b] generally taken as the standard deviation of the mean
[c] treated as a uniform probability distribution [16]

6.3 Low Conductivity Standards

The absorption of CO_2 into low conductivity solutions must be limited to reduce the uncertainty of the standard. This is achieved by using a mixed aqueous-nonaqueous solvent.

Sec. 2.3 discussed the expected variability in the conductivity of a solution based on variations in the atmospheric content of CO_2. If the 5 µS/cm solution were prepared with KCl in water, the expected variation in conductivity would be ± 0.2 µS/cm (4 %, relative). However, when the solution is prepared using a mixed aqueous-nonaqueous solvent, the CO_2 effect is 0.1 µS/cm (2 %, relative) [8]. Therefore, to lower the effect of CO_2 on the solutions, the 5 µS/cm and 15 µS/cm SRMs consist of KCl in 30 % n-propanol 70 % water.

A list of the molality and mass fraction for each nominal value of the SRMs is given in Table 10.

Table 9. Molality and Mass Fraction (Given in Grams Solute per Kilogram Solution, In Vacuum) of Low Conductivity SRMs in 30 % n-PrOH-H_2O[8]

κ/(µS/cm)	Potassium Chloride (KCl)	
	molality/(10^{-3} mol/kg)	w/(g/kg)
5.00	0.072 9	0.005 43
15.0	0.230	0.017 1

7. Storage of Solutions

The length of time for storage of conductivity solutions must be considered when determining the appropriate container for the solution. The instability of a solution in a given package for a given time period is the main factor in determining the appropriate container. Instability may be caused by transpiration, evaporation, or leaching. Transpiration is the passage of solvent through the container. Evaporation occurs through the space between the bottle and the cap, usually resulting from the cap relaxing and loosening with time. Leaching of ions from the container or reactions of the solution with the container may also occur. All of these effects cause the solution to be unstable. The instability of the solution must be considered when determining the conductivity of the solution. Evaporation, transpiration, and leaching cause the conductivity of the solution to increase with time. To obtain an accurate measurement of the conductivity of a solution, transpiration, evaporation, and leaching must be minimized. Over time, if instability of the solution occurs, the accuracy of the conductivity measurement will be compromised.

7.1 Plastic Containers

High density polyethylene (HDPE) bottles (opaque white) were examined for solutions having a nominal conductivities of 5 µS/cm and 15 µS/cm (both KCl in 30 % n-propanol 70 % water), and 100 µS/cm and 500 µS/cm (both KCl in water). The changes in conductivity of the solutions over time are given in Table 10. The HDPE bottles containing the 5 µS/cm and 15 µS/cm solutions had turned yellow by 12 months and 16 months, respectively. The change in the color of the bottle is presumed to be a reaction of the n-propanol with the HDPE, since the color change did not occur with purely aqueous solutions. HDPE bottles were unacceptable for 5 µS/m and 15 µS/cm solutions.

Teflon bottles were also examined for solutions having nominal conductivities of 5 µS/cm (KCl in 30 % n-propanol 70 % water) and 100 µS/cm (KCl in water). The relative increase in κ, 59 % at 5 µS/cm (5 months) and 7.5 % at 100 µS/cm (6 months), was also unacceptable.

Table 10. HDPE Stability Studies

5 µS/cm		15 µS/cm		100 µS/cm		500 µS/cm	
time[a]/ months	% κ increase	time[a]/ months	% κ increase	time[a]/ months	% κ increase	time[a]/ months	% κ increase
0	0	0	0	0	0	0	0
3.0	2.7	3.2	1.0	2.9	0.29	3.1	0.03
6.4	8.9	6.0	2.3	6.6	0.33	6.1	0.04
9.4	23.1	9.0	6.5	9.0	0.42	9.1	0.04
12.1	38.4	13.7	12.7	12.1	0.34	12.3	0.06
16.0	64.2	17.2	19.7	16.0	0.47	16.6	0.06
19.9	94.9	19.7	24.4	20.4	0.47	20.0	0.14
23.9	119.2	24.0	34.6	25.2	1.24	24.2	0.09

[a] Approximate number of months since the initial measurements of the batch where the initial measurement occurred at 0 months.

7.2 Glass Containers[1]

An extensive study of the change in conductivity of solutions (5 µS/cm, 15 µS/cm, 100 µS/cm, 500 µS/cm, 1000 µS/cm, 100 000 µS/cm) stored in glass containers (screw-capped bottles[2], ampoules[3], and serum bottles[4]) has been conducted [20]. Leaching (not evaporation or transpiration) was significant for solutions having $\kappa \leq 100$ µS/cm. The largest source of instability for the high-conductivity solutions ($\kappa \geq 500$ µS/cm) may be either leaching (serum bottles) or evaporation (screw-cap bottles), depending on container type and size.

7.3 Container Choice

For solutions that will be used immediately after they are prepared, such as primary standards, all of the instability issues are insignificant. The most convenient container for preparation of the solutions is HDPE or low-density polyethylene (LDPE). The plastic containers may also aid in the equilibration of CO_2 by allowing CO_2 to pass through the walls of the bottle to the solution.

Solutions that will be stored for more than a day, such as an SRM, should be packaged such that minimal change in conductivity occurs over the time of storage. In this laboratory, HDPE

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[1] Certain materials are identified in this section in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

[2] Screw-capped bottles specifically refer to Corning #1395. Other screw-capped bottles may behave differently based on the composition of the glass and/or the screw-cap.

[3] Ampoules specifically refer to Wheaton #176784. Other ampoules may behave differently based pm the composition of the glass.

[4] Serum bottles specifically refers to bottles having Wheaton #223747. The septa used for the bottles were Wheaton #224168. Other serum bottles may behave differently based on the composition of the glass and/or the closure.

bottles are used for SRM 3190 (dilute HCl) and glass containers are used for all other conductivity SRMs.

High-density polyethylene (HDPE) bottles are used for the storage of SRM 3190 (25 μS/cm), a dilute HCl solution. The effect of transpiration through the plastic has been noted in this laboratory. To minimize cap relaxation, the capped bottle is dipped in beeswax. To minimize the long-term effects of transpiration, the bottle is sealed in an air-tight, aluminized bag. Both of these effects cause the conductivity of the SRM to increase. This observed increase from previous lots of this SRM has ranged from 0.005 (μS/cm)/month to 0.07 (μS/cm)/month.

The containers chosen for packing all of the other conductivity SRMs were chosen based on which container provided the most stability for the solution. SRM 3198, 3199, and 3191 (5 μS/cm, 15 μS/cm, and 100 μS/cm, respectively) are currently packaged in screw-cap bottles, which provide the largest volume to surface area ratio and therefore the least noticeable leaching. SRM 3192, 3193, 3194, 3195 and 3196 (500 μS/cm, 1000 μS/cm, 10 000 μS/cm, 20 000 μS/cm, and 100 000 μS/cm) are currently packaged in ampoules, which eliminate evaporation and transpiration and have only minor leaching. The evaluation of packaging for solutions having conductivity values between 100 μS/cm and 500 μS/cm was not completed. The optimal point to switch from ampoules to screw-cap bottles occurs at a κ value between 100 μS/cm and 500 μS/cm but its exact value was not more thoroughly examined.

8. Discussion and Conclusion

The various standards described in this report provide several options for cell calibration. The primary standards are used for the highest accuracy work. Other standards are used as needed to calibrate the conductivity cells. In some cases the conductivity of an intermediate standard must be determined as well.

The SRMs are issued in a form that is easy to use at the expense of high accuracy. The conductivity of the solvent in equilibrium with atmospheric CO_2 is included, which causes a somewhat higher uncertainty. The low conductivity standards are intended for water quality control. To lower the CO_2 effect on the lowest conductivity solutions, 30 % n-propanol 70 % water mixed solvent is used in which the CO_2 effect is minimal.

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