

# Ultrapure Water – The Standard for Resistivity Measurements of Ultrapure Water

**Anthony C. Bevilacqua, Ph.D.<sup>1</sup>**  
**Thornton Associates, Inc.**  
1432 Main Street  
Waltham, Massachusetts 02154  
Phone (781) 890-3399  
Phone (800) 642-4418  
FAX (781) 890-5507  
email abevilacqua@thorntoninc.com

## **Abstract**

For years, resistivity/conductivity<sup>2</sup> instrumentation has been used as a reliable indicator of ionic water quality, especially for ultrapure water (UPW). Traditionally, the instrumentation is procured, installed, powered up, and perhaps connected to a PLC, strip chart recorder, or a LAN. After that, the instrument and sensor receive no attention until a problem arises. Today, continuous calibration and verification are key elements in any QC and QA program. In recent years, users have been using standard solutions to calibrate sensors. However, a major complaint is that these solutions are not in the user's operational range, and thus are not ideal standards. Numerous standard solutions have been proposed, but none possess all of the desirable requirements : ease-of-preparation, resistivity value in the range of operation, impervious to air and other contamination, and verifiable.

During the last several years, as a result of our investigations into the relationship between resistivity and temperature for UPW, we have developed a methodology for calibration that meet all of the criteria stated above. We will provide data to support 5 primary conclusions :

1. The relationship between temperature and resistivity for UPW is well known.
2. Resistivity sensors (for use in UPW) can be calibrated in high conductivity ASTM standard solutions under

---

<sup>1</sup> Please see Acknowledgements for complete listing of contributors.

<sup>2</sup> Resistivity and conductivity are identical measurements, differing only in the units of expression. Those involved in the production of semiconductor grade high-purity water use resistivity units, i.e., 18.2 MΩ-cm. Power plant chemists and the pharmaceutical industry tend to prefer conductivity units such as μS/cm or μmho/cm. 0.1 μS/cm = 0.1 μmho/cm = 10 MΩ-cm. Neither terminology is exclusive. The remainder of the paper will utilize both terms depending on the application, but both terms are always applicable.

*appropriate instrument conditions.* Despite this, there is a need for standard solutions in the 0.1 to 50 M $\Omega$ -cm range.

3. Resistivity sensors (for use in UPW) are ideally calibrated in UPW at varying temperatures. This method validates itself by confirming that the water is pure (<0.2 ppb).
4. UPW is a fundamental resistivity standard.
5. Resistivity sensors require infrequent calibration.

## **Introduction**

There are numerous critical reasons for the need for calibration of instrumentation. The most common reason is to know that the displayed value is the actual value (to within some specified tolerance). But in the numerous industries where high purity water is utilized, there are other varied reasons. For example, in power generation facilities, the water chemistry is tightly controlled by knowledge of the resistivity/conductivity and pH. In this case, small excursions from established operating parameters cause significant increases in downtime, maintenance, and cost. In pharmaceutical industries, there are strict regulatory requirements that are prescribed by the U.S. Pharmacopeia and enforced by the Food and Drug Administration for the manufacture and use of Purified Water and Water for Injection. Resistivity instruments are required to meet very specific calibration requirements for use in these water systems so as to maintain a minimum level of control over these water systems. In microelectronics industries, the need for calibration is self-imposed in order to produce higher quality water for the manufacture of faster and denser devices. However, because of the unique relationship between ions and resistivity, accurate and precise knowledge of the resistivity is a key to the limit of detection (LOD) for ionic impurities.

Regardless of the different motives for the use of resistivity in ultrapure water systems, calibration is needed. In all cases, there has been one issue that has consistently presented a significant conundrum for the user – the lack of a calibration standard in the resistivity range of interest, namely any resistivity above 0.1 M $\Omega$ -cm (below 10  $\mu$ S/cm). *Therefore, the focus of this paper is 1) the description of the problems associated with standards at this purity level and 2) the declaration of a new fundamental standard for use in pure waters - and that standard solution is ultrapure water.*

## **Need for Calibration**

Resistivity is the single most common measurement in every on-line high purity water system. Advances in measurement capability and the inherent sensitivity of resistivity to ionic contamination in ultrapure water (UPW) has forged resistivity instrumentation into the front-line indicator of ionic contamination by reliable and cost-effective means. While the various forms of ion chromatography and mass spectrometry offer the most sensitive means of detection and speciation, these methods remain somewhat prohibitive insofar as immediate response, sample preparation time, sample handling, and capital costs are concerned. Meanwhile, there is no dispute to the fact that the most common metals (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, etc...) and other electroanalytically detectable species (H<sup>+</sup>, OH<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>,

$\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , etc...) are found in water systems at trace levels. Further, they are most rapidly and inexpensively detected by resistivity, though not at the detection limits of research-grade IC and MS instrumentation. These species are found in the best semiconductor grade water systems at concentrations below 100 ppt (1 ppt = 1 ng/L).

### Resistivity Limit of Detection

The inability of resistivity to speciate turns out to be a benefit since the sum of all ionically-active species become detectable. This is the basis for using resistivity as the primary means of ion impurity detection. For further validation of the sensitivity and simplicity of resistivity, one needs to look no further than on-line TOC instrumentation. Although the oxidation technologies differ, resistivity is the exclusive and most sensitive means of sub-ppb TOC detection<sup>3</sup>.

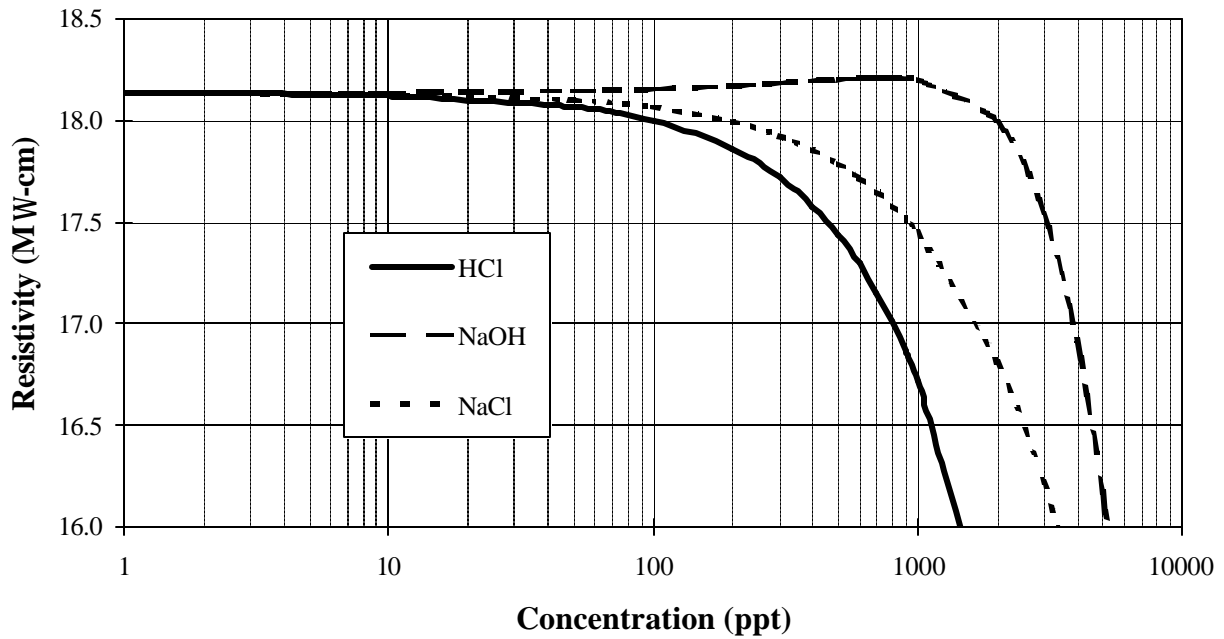
To illustrate the variety of detectable species, the resistivity of three different common chemicals - an acid, base, and salt - at very low concentrations at 25°C are shown in Figure 1. At very low contaminant concentrations, 1-10 ppt, the resistivity is virtually unchanged. It is only at concentrations exceeding 100 ppt that acid and salt species lower the resistivity so that it is discernable from a 1-10 ppt contaminant. And if the contaminant is slightly basic (NaOH impurity), then there is a slight increase in the resistivity until ~1000 ppt (1 ppb)!

Figure 2 shows the sensitivity that is required to detect different concentrations of chemical species at 25°C. Under the best conditions, resistivity systems are capable of measuring to ~1% reliably in *real water systems*, thus making detection of ~250 ppt (as NaCl or 120 ppt in the acid form) very possible and practical. At higher temperatures, these concentrations become more difficult to detect. This is discussed later.

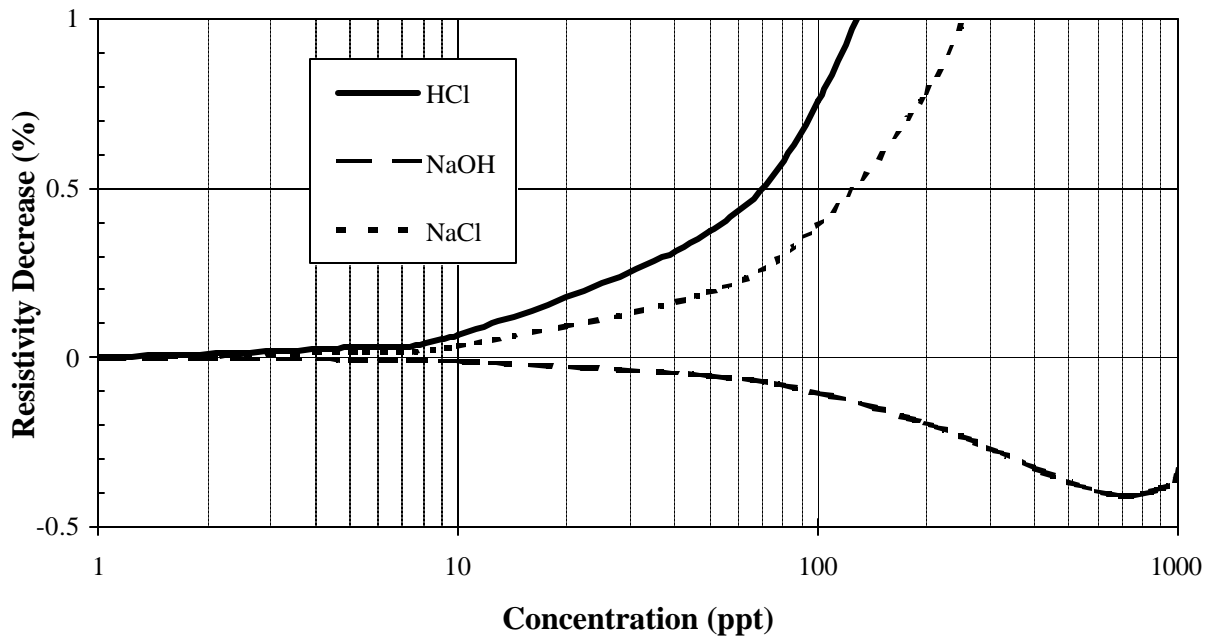
---

<sup>3</sup> The most common methods of TOC measurement are not based on the direct measurement of carbon, but they are based on its conversion to its highest, stable oxidative state, carbon dioxide ( $\text{CO}_2$ ).  $\text{CO}_2$  is detected by FTIR down to ~25 ppm while  $\text{CO}_2$  is detected by resistivity (in the form of the dissociative products of  $\text{H}_2\text{CO}_3$ ) as low as 50 ppt.

**Figure 1. Resistivity at Trace Concentrations of Three Common Impurities at 25°C**



**Figure 2. Required Sensitivity for Trace Concentrations by Resistivity Methods at 25°C**



The ability to detect the lowest concentrations of ionic species is controlled by three factors :

- the specific conductance of the ions
- the sensitivity of the instrumentation
- the absolute calibration of the resistivity system

The conductance of each ion species is a physical-chemical property of the ion (which cannot be altered), although its temperature-dependence can be exploited. In some cases, some chemical species, notably the transition and heavy metals, are not detectable because of their insufficient ionic character. But these are not the prevalent ionic impurities as listed above. The sensitivity of modern resistivity instrumentation is on the order of 0.1% of value and can approach 0.01%, so it is not this factor that impacts the LOD for resistivity. If this were the limiting factor, then LODs near 1-10 ppt could be achievable by resistivity.

The primary factor that keeps the resistivity LOD above 100 ppt is the limited ability for absolute calibration of the system (meter, sensor, and cable). Without calibration, the relationship between the resistivity and the purity of water is unknown. Similarly, without calibration, the relationship between the resistivity and temperature for ultrapure water is unknown.

### “Quality” Requirements for Calibration

In the microelectronics industry, there are no governmental regulatory requirements for the production of water to rinse and clean wafers. Pure water requirements are driven by technological advancements and market needs, i.e., cleaner water provides faster and more closely spaced devices. In cases such as these, control of the water system is required to maintain the quality of water system, and the control of the water system rests, in part, on the calibration of the resistivity system.

A resistivity system that requires frequent calibration means additional laborious steps by the water system operator to maintain accurate knowledge of the water system. If the resistivity system is constantly out of calibration, then the water system may also be out of control. At the very least, there is uncertainty.

### Calibration

Detailed issues pertaining to calibration have been described at this conference previously[1]. Briefly, in any resistivity system, there are three components to calibrate:

- Meter and cable
- Temperature sensor
- Conductivity sensor

The meter and cable are readily calibrated by replacing the sensor with a series of calibrated, NIST-traceable resistors<sup>4</sup> (or decade box) and insuring that the instrument measures AC resistances accurately. By placing the

---

<sup>4</sup> Most on-line process control resistivity instruments have 2 or more measurement circuits in order to provide a wide dynamic measurement range. To insure accurate measurement across calibration of the entire measurement circuitry, all measurement ranges should be calibrated. This usually requires as many calibrated resistors as measurement circuits.

decade box at the end of the cable, as long as 500 feet, any additional impedance in the cable is accounted for in the calibration. Modern resistivity instrumentation will have menu-driven instructions to allow the user 1) to verify and 2) to automatically rectify any differences.

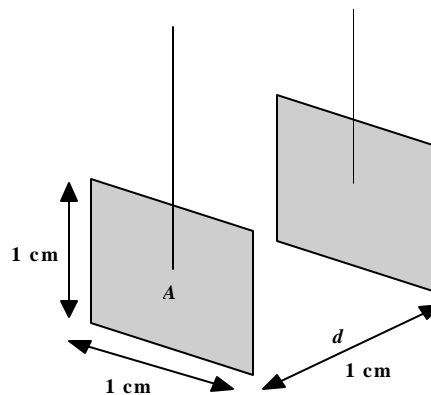
Likewise, the temperature device is calibrated by placing the sensor in the same fluid as a precise temperature standard. The required accuracy of the temperature standard depends on the desired accuracy of the compensated resistivity measurement[2,3]. If a calibrated temperature standard is not available, an ice-water mixture is an ideal standard. Use clean ( $<10\mu\text{S}/\text{cm}$ ) water to prepare the ice-water mixture in a container. Place this container in a salt-water-ice mixture to insure that the inner ice-water mixture is at  $0^\circ\text{C}$ . As above, modern resistivity instrumentation will have the full capability to verify and rectify any differences.

The final component to calibrate is the resistivity sensor. This represents the most problematic portion of the calibration and the crux of this paper. *Calibration of the sensor is also known as determination of the cell constant.*

### Cell Constant

The accurate determination of the resistivity cell constant can be quite difficult in actual practice. Conceptually, the cell constant is sometimes idealized as two  $1\text{ cm}^2$  plates (area,  $A$ ) that are separated by  $1\text{ cm}$  (distance,  $d$ ) as shown in Figure 3.

**Figure 3. Conceptual Drawing  
of Cell Constant**



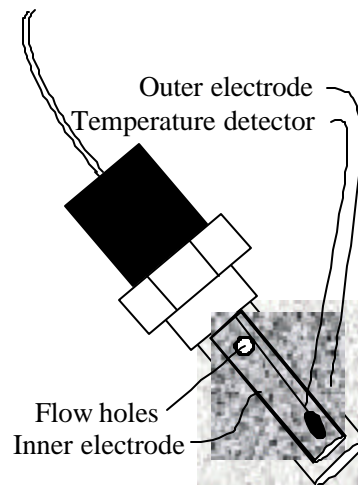
The resistance of the water between the electrodes is the value measured by the meter. Since the resistance will increase with  $d$  and decrease with  $A$ , the resistance is normalized for these geometrical factors in order to measure the ionic quality, or resistivity, of the water. These geometrical or normalization factors are combined into one term called the cell constant,  $\phi$ . For the general case,  $\phi$  is defined in eq (1).

$$\phi = l/A \text{ with the units of } \text{cm}/\text{cm}^2 \text{ or } \text{cm}^{-1} \quad (1)$$

For the configuration in Figure 3,  $\phi$  is  $1\text{ cm}^{-1}$ . While an accurate measurement of the cell dimensions could yield the cell constant, there are some factors that make this approach impractical[4]. First, this square plate model does not have the mechanical stability for in-line process applications. Sensors with concentric electrodes (Figure 4) have become the most common design for in-line pure water applications. However, this design, and the associated flow

holes, do not lend themselves to dimensional analysis because of the fringe effects from the electrical measurement field at the flow holes and the end of the concentric electrodes. This makes accurate definition of the effective area improbable.

**Figure 4. Modern Concentric Cell Design**



Variations in manufacturing tolerances may approach 1 to 2% for the highest quality sensors, but 5-10% is not uncommon among some manufacturers. Further, the metal/liquid interface impedance is affected by variations in surface finish of the electrodes, which are also subject to manufacturing processes. ***Where high accuracy is required, a post-manufacturing calibration procedure to determine the cell constant is mandatory.***

### Limitations of Existing Standard Solutions

The only practical method available to accurately determine the cell constant to 1% accuracy or better is by measuring the resistance of a standard reference solution<sup>5</sup>. The resistivity of the reference solution must be known with high certainty at the measurement temperature and the uncompensated resistivity and temperature of the fluid must be precisely measured. The cell constant is then determined by<sup>6</sup>:

$$\phi = \frac{\text{Measured Resistance } (\Omega)}{\text{Reference Solution Resistivity } (\Omega\text{-cm})} = \text{cell constant } (\text{cm}^{-1}) \quad (2)$$

The basic reference standards for resistivity have been the KCl solutions originally devised by Kohlrausch in the 1890s, refined by Bradshaw and Jones[5], and adopted by ASTM in Test Method D1125[6]. These solutions are prepared with excellent accuracy and high reliability by a qualified chemist. Solutions C and D, as described in ASTM D1125, are included in Table 1. Also included in Table 1 are six Standard Reference Materials (SRMs) offered by the National Institute of Standards and Technology (NIST) with conductivities of 1,000  $\mu\text{S/cm}$  or less. These are

<sup>5</sup> Actually, another practical calibration method is to place it in the same solution as another standard sensor. Of course, the original standard sensor must be calibrated in a standard solution.

<sup>6</sup> This calculation is transparent to the user in most modern process resistivity instrumentation. While meters measure resistance, they only display resistivity after adjustment for the cell constant. The resistivity system measures the resistance. The user enters the reference solution resistivity or conductivity. The instrument then calculates the cell constant.

provided as ready-to-use solutions in sealed 500 mL containers, but at considerable expense, currently \$319 US.

**Table 1. List of Standard Solutions**

Standard	Conductivity @ 25.0°C ( $\mu\text{S}/\text{cm}$ )	Comp.*	Air Content	Uncertainty ( $\mu\text{S}/\text{cm}$ )	Uncertainty (%)	Date
ASTM D1125 solution D	146.93**	KCl in water	Equil.	0.3	0.2	1995
ASTM D1125 solution C	1408.8**	KCl in water	Equil.	1	0.07	1995
NIST SRM 3198	5	KCl in 30% 1-propanol	Equil.	0.12 <sup>‡</sup>	2.4 <sup>‡</sup>	12/94
NIST SRM 3199	15	KCl in 30% 1-propanol	Equil.	0.12 <sup>‡</sup>	0.8 <sup>‡</sup>	12/94
NIST SRM 3190	25	HCl in water	Equil.	0.3 <sup>‡</sup>	1.2 <sup>‡</sup>	2/95
NIST SRM 3191	100	KCl in water	Equil.	0.24	0.24	2/96
NIST SRM 3192	500	KCl in water	Equil.	0.26	0.05	7/95
NIST SRM 3193	1000	KCl in water	Equil.	0.4	0.04	6/96
Pure water <sup>†</sup>	0.03138 @ 15°C	water	CO <sub>2</sub> -free	0.00008	0.25	
Pure water <sup>†</sup>	0.05501 @ 25°C	water	CO <sub>2</sub> -free	0.00013	0.25	
Pure water <sup>†</sup>	0.11301 @ 40°C	water	CO <sub>2</sub> -free	0.00028	0.25	

\* All standards are made with deionized water.

\*\* Plus the conductivity of the water used to prepare the solution

† These solutions require a closed-loop, recirculating deionized water system.

‡ NIST has recently increased the uncertainty. The values stated in the Table are lower uncertainties. The new uncertainties are higher.

The uncertainties of the low conductivity (<100  $\mu\text{S}/\text{cm}$ ) NIST SRMs are greater than uncertainty of ASTM Solution D, and often beyond the accuracy tolerances required for ultrapure water applications. Further, the use or re-use of these low conductivity standards that have been subjected to airborne and atmospheric contaminants, notably CO<sub>2</sub>, may render the previously opened SRM unreliable and introduce further uncertainty[7].

The ASTM solutions offer acceptable accuracy and are much less susceptible to contamination, but they are outside the range of the user's operation. Normally, this raises a concern to the user or the QA Manager, regardless of the range of the instrument. Later in this paper, we will demonstrate the ability to use ASTM solutions as viable reference solutions, even for UPW application. Despite this evidence, most users still prefer a "standard reference solution" in the range of normal process operation.

In summary, resistivity sensor manufacturers, metrology laboratories, and others that have a critical need to very accurately determine and calibrate resistivity cell constants for sensors designed to measure pure and ultrapure water have been faced with a dilemma. To date, the alternatives have been to use either :

- reference solutions approaching the pure water range, but lack the precision desired or
- highly accurate standards that are outside the measurement range of interest



Clearly, another approach has been needed.

## Ultrapure Water as a Fundamental Standard

### Measurement of the Resistivity of Pure Water from 0-100°C

An inherent physical property of a *pure substance* is its resistivity at specific temperatures. In the 1980's, scientists at Thornton Associates began to collect data to establish the resistivity of pure water over a temperature range of 0° to 100°C. Pure water has a very high, but not quite infinite, electrical resistivity. At 25°C, the accepted value and uncertainty[2,4] for the resistivity,  $\rho$ , and its reciprocal, conductivity,  $\kappa$ , are:

$$\kappa = 0.05501 \pm 0.00009 \mu\text{S}/\text{cm at } 25.00^\circ\text{C} \quad (4)$$

Further data on the established fundamental physical parameters of pure water are taken from previous work[2] and provided in Table 2 at 5°C intervals.

**Table 2. Fundamental Ion-Related Properties of Water**

Temp (°C)	Density (g/cm <sup>3</sup> )	K <sub>w</sub> (molar)	I <sub>H<sup>+</sup></sub> (S·cm <sup>2</sup> /mol)	I <sub>OH<sup>-</sup></sub> (S·cm <sup>2</sup> /mol)
0	0.999770	1.156×10 <sup>-15</sup>	225.0	118.4
5	0.999949	1.872×10 <sup>-15</sup>	250.3	133.8
10	0.999728	2.964×10 <sup>-15</sup>	275.4	149.7
15	0.999155	4.573×10 <sup>-15</sup>	300.3	165.9
20	0.998272	6.878×10 <sup>-15</sup>	324.9	182.5
25	0.997113	1.011×10 <sup>-14</sup>	349.2	199.2
30	0.995708	1.455×10 <sup>-14</sup>	373.0	216.2
35	0.994080	2.055×10 <sup>-14</sup>	396.4	233.2
40	0.992250	2.854×10 <sup>-14</sup>	419.2	250.2
45	0.990233	3.898×10 <sup>-14</sup>	441.4	267.2
50	0.988041	5.245×10 <sup>-14</sup>	463.0	284.3
55	0.985684	6.957×10 <sup>-14</sup>	483.9	301.3
60	0.983171	9.104×10 <sup>-14</sup>	504.1	318.2
65	0.980506	1.176×10 <sup>-13</sup>	523.7	335.1
70	0.977696	1.501×10 <sup>-13</sup>	542.5	352.0
75	0.974745	1.893×10 <sup>-13</sup>	560.6	368.9
80	0.971659	2.362×10 <sup>-13</sup>	578.0	385.8
85	0.968445	2.917×10 <sup>-13</sup>	594.7	402.8
90	0.965109	3.567×10 <sup>-13</sup>	610.7	420.0
95	0.961664	4.321×10 <sup>-13</sup>	626.1	437.4
100	0.958121	5.189×10 <sup>-13</sup>	640.9	455.1

The experimental data was fit to a 5<sup>th</sup> order exponential

$$\rho = 1/\kappa = \exp(a_0 + a_1 T^1 + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5) \quad (5)$$

where

$$\begin{aligned}
 a_0 &= 4.45656 & a_1 &= -7.33064 \times 10^{-2} & a_2 &= 5.02097 \times 10^{-4} \\
 a_3 &= -2.56203 \times 10^{-6} & a_4 &= 6.43445 \times 10^{-9} & a_5 &= 1.40405 \times 10^{-12}
 \end{aligned}$$

The quality of the experimental data has been independently verified by comparing it to the theoretical resistivity/conductivity of pure water that can be determined from basic fundamental properties of water according to eq (6) and Table 2.

$$\kappa \text{ (S/cm)} = 1/\rho = 10^{-3} d (C_{H^+} \lambda_{H^+} + C_{OH^-} \lambda_{OH^-}) = 10^{-3} d K_w^{1/2} (\lambda_{H^+} + \lambda_{OH^-}) \tag{6}$$

where d is the specific gravity, C<sub>i</sub> is the concentration of ion i (mole/L) determined from the dissociation of H<sub>2</sub>O, K<sub>w</sub>, and λ<sub>i</sub> is the specific conductance of ion i (S-cm<sup>2</sup>/mole). Each variable is temperature dependent. The relevant fundamental values of H<sub>2</sub>O are listed[8,9] in Table 2. Each has been determined independent of pure water resistivity measurements.

The resistivity of pure water (based on fundamental properties of water) can then be calculated using eq (6) and values from the literature as a function of temperature. A summary of the calculated (theoretical) and recently-measured[2] values for pure water at 5°C intervals is provided in Table 3.

**Table 3. Resistivity of UPW from Fundamental Properties and Experiment**

Temp (°C)	UPW Experimental Data Resistivity (MW -cm)	UPW Experimental Data Conductivity (mS/cm)	UPW Theoretical Data Resistivity (MW -cm)	Diff (%)
0	86.19	0.01160	86.07	0.14
5	60.48	0.01654	60.27	0.35
10	43.43	0.02302	43.26	0.41
15	31.87	0.03138	31.75	0.37
20	23.85	0.04193	23.78	0.29
25	18.18	0.05501	18.14	0.19
30	14.09	0.07098	14.07	0.10
35	11.09	0.09019	11.08	0.03
40	8.85	0.1130	8.85	-0.02
45	7.15	0.1398	7.16	-0.06
50	5.85	0.1709	5.86	-0.09
55	4.84	0.2066	4.85	-0.12
60	4.04	0.2474	4.05	-0.17
65	3.41	0.2935	3.42	-0.24
70	2.90	0.3453	2.91	-0.34
75	2.48	0.4030	2.49	-0.46
80	2.14	0.4668	2.16	-0.62
85	1.86	0.5369	1.88	-0.78
90	1.63	0.6134	1.65	-0.92
95	1.44	0.6961	1.45	-1.01
100	1.27	0.7848	1.29	-1.00

*The agreement between the experimental data and the theoretical data is provided in the last column. The*

*satisfactory agreement provides independent verification that the experimental methods are accurate, and they may be superior in light of the known inaccuracies that are indigenous to high-temperature OH conductance measurements.*

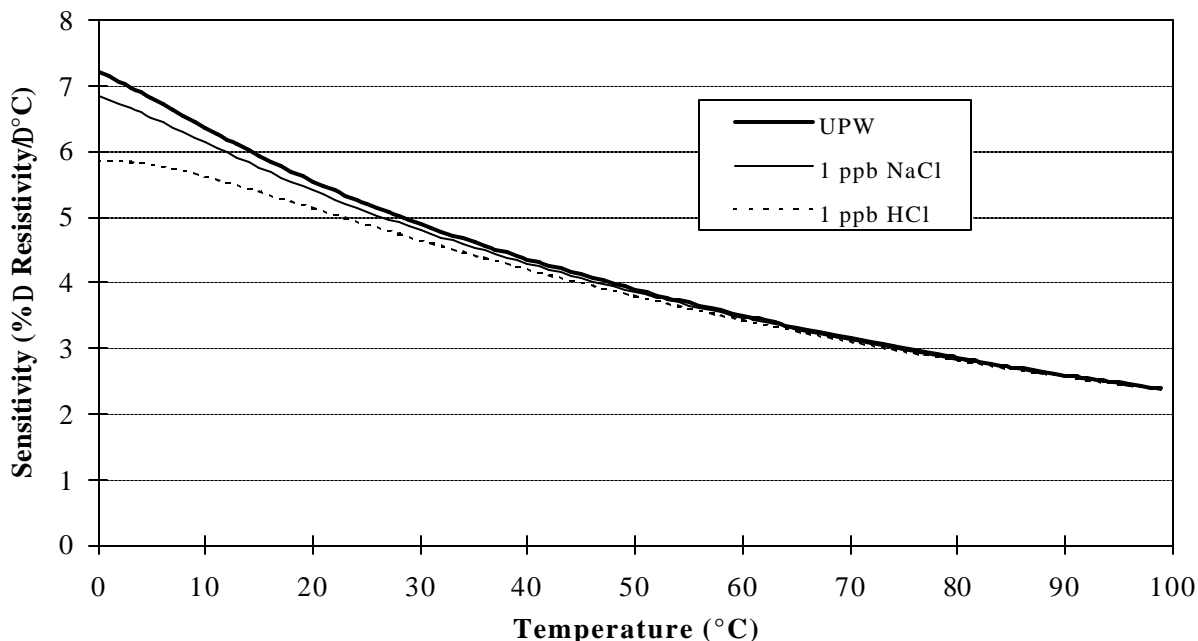
### Sensitivity of the Conductivity of UPW as a Function of Temperature

A particularly important property of pure water is its unique resistivity/temperature dependency. We define this sensitivity,  $S_T$ , according to eq (7).

$$S_T = 100 \left( \frac{\partial \rho}{\partial T} \right)_T \left( \frac{1}{\rho} \right)_T \tag{7}$$

The sensitivity or temperature coefficient of ultrapure water varies considerably from 0100°C and decreases dramatically as the temperature increases as shown in Figure 5.

**Figure 5. Sensitivity to Temperature for UPW, 1 ppb NaCl, and 1 ppb HCl**



The specific conductivity of NaCl is also well known as a function of temperature. The general equation relating the conductivity to concentration is provided in eq (8).

$$\kappa = 1/\rho = 10^{-3} d \sum_i^{\text{all ions}} C_i \lambda_i \tag{8}$$

From these equations, the resistivity of water with low ionic impurities can be easily determined, as can the sensitivity of these solutions to temperature. The sensitivities of the resistivity to temperature for UPW and UPW with 1 ppb NaCl (or 1 ppb HCl) impurity are shown in Figure 5. ***The most critical feature is that, at any temperature, pure water has greater sensitivity to temperature change than any water containing an ionic solute.***

The differences in sensitivity provide the basis for the remainder of the paper. Table 4 shows that the resistivity decrease with a 1 ppb impurity of NaCl (or any other impurity) does not uniformly decrease the resistivity of water at all temperatures. For example, at 15°C, a 1 ppb NaCl impurity causes a 6% decrease in the resistivity, while the same impurity causes a 1.5% decrease at 75°C. *It is the enhanced resistivity-temperature sensitivity for cold UPW that we exploit to prove that the water is pure and acceptable for use as a fundamental standard.*

**Table 4. Decrease in Resistivity as a Function of Temperature**

	15°C		25°C		40°C		75°C	
	Res. (MW -cm)	decrease (%)	Res. (MW -cm)	decrease (%)	Res. (MW -cm)	decrease (%)	Res. (MW -cm)	decrease (%)
UPW	31.87		18.18		8.850		2.481	
1 ppb NaCl	30.08	5.97	17.45	4.17	8.628	2.60	2.444	1.54

Figure 5 and Table 4 show that as temperature increases, impurities are harder and harder to detect[1]. We take advantage of the converse at lower temperatures - impurities are easier to detect - to provide multiple standard reference solutions for resistivity based on the physical properties of water and solutes at infinite dilution.

If three determinations of the cell constant are made at three different (and accurately known) temperatures, and the calculations of the cell constant are within the accuracy of the instrument and sensor,  $\pm 1.0\%$  with our instrumentation, then the cell constant is correct and the water is free of ionic contaminants. *Therefore, since the resistivity of pure water is a fundamental physical characteristic of the pure substance, we suggest that pure water be used as the reference solution for UPW and other high resistivity applications.*

## Experimental Data

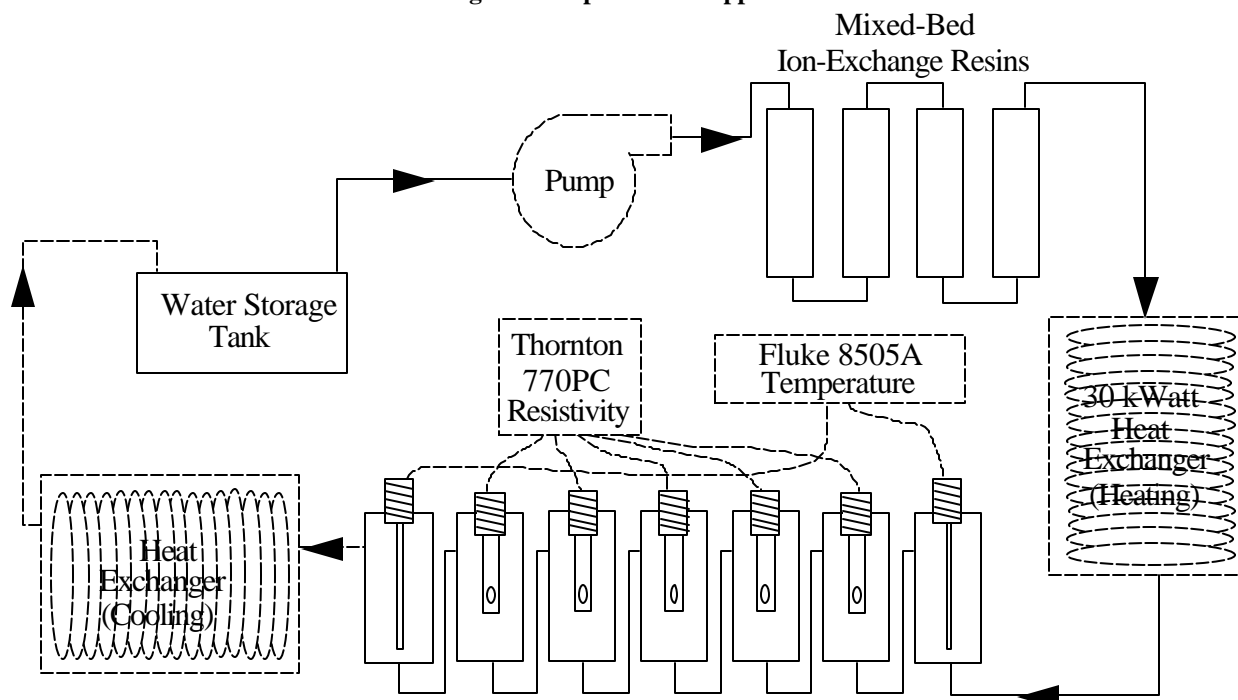
### Experimental Considerations

We have manufactured and tested a resistivity system[2] that incorporates all of the design criteria that are required to achieve minimum resistivity error. Sensors have undergone careful calibrations and are designed for maximum thermal response. Class A 1000  $\Omega$  Pt RTDs are used and the sensor is constructed with a 90% thermal response time of 15-25 seconds. Portions of the sensor exposed to the ambient are insulated. Meters have had temperature and resistivity measurement circuits calibrated on all ranges, including calibration of the cables. All resistance measurements are 3-wire which automatically corrects for cable resistance. Other features in the circuit design are applied to minimize self-heating due to measurement current through the RTD.

We have built a small UPW system (see Figure 6) that prepares 18.2 M $\Omega$ -cm (0.0550  $\mu$ S/cm) water at 25°C repeatably and reliably. In fact, for any temperature from 0-100°C, the resistivity of a pure water system is known precisely[2]

according to eq 5. The water is prepared in a closed-loop, recirculating water system with the sensors located after a series of nuclear grade, mixed-bed ion-exchange resins. The entire system consists of Teflon and PVDF tubing.

**Figure 6. Experimental Apparatus**



To heat the UPW, it passes through a titanium 30 kW heat exchanger after the polisher to achieve the desired temperature, then to the sensors for measurements, then through 50 feet of Teflon tubing. This tubing is immersed in cold municipal water to dissipate the heat. The UPW returns to the storage tank where it is re-circulated back to the polishers. This "polish-heat-measure-cool" cycle is required to prevent overheating and degradation of the ion-exchange resins. The water quality was verified by monitoring the compensated resistivity of the cooled water.

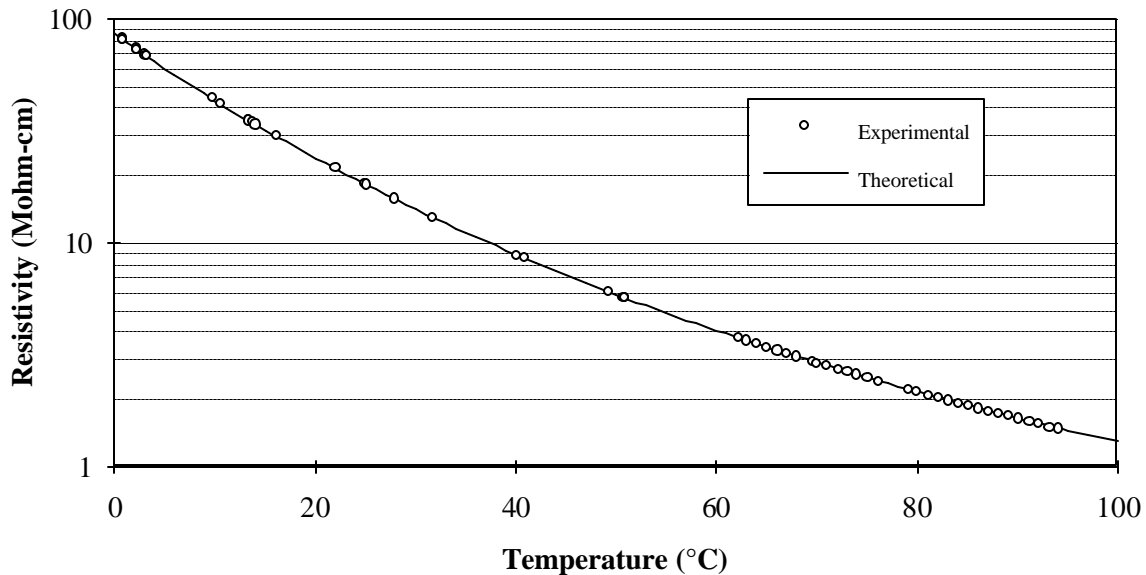
The temperature at each resistivity sensor is monitored by 1000  $\Omega$  Pt RTDs at the entrance and exit ends of the resistivity measurement portion of the water loop. The RTDs were calibrated to 0.01°C accuracy from 0 to 100°C by an external calibration facility. The RTD resistance was measured by a Fluke 8505A multimeter and converted to temperature[10]. As much as a 1°C reduction in temperature occurs across the loop due to ambient cooling, so the temperature at each resistivity sensor was determined by linear interpolation across the measurement loop. The resistivity of each sensor was measured using Thornton 770PC meters with the aforementioned features. Data was collected over a LAN and stored to disk for subsequent processing.

## Experimental Results

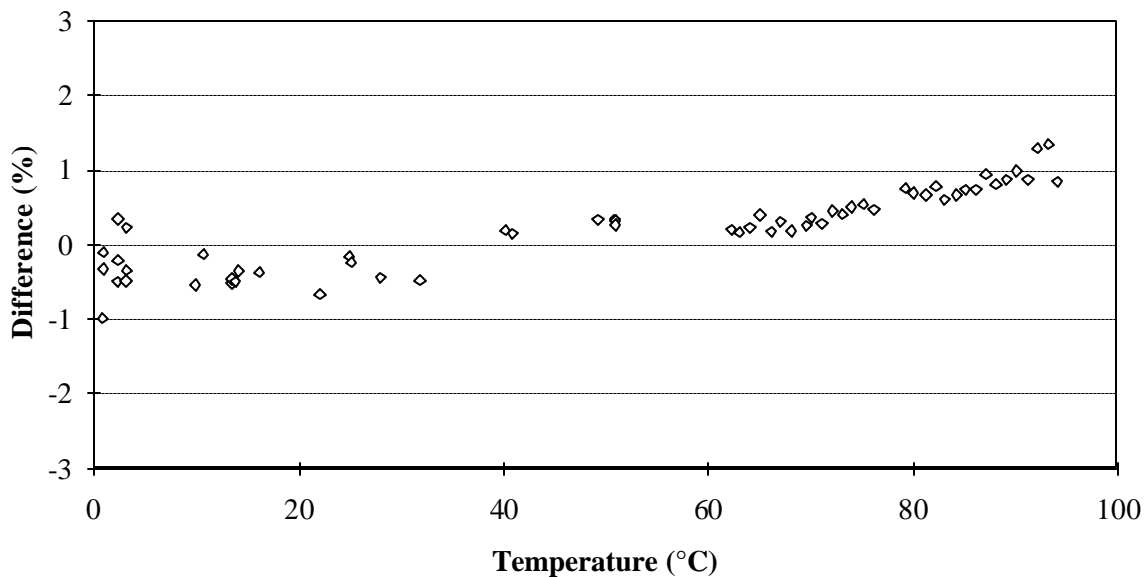
A fraction of the data collected from 5 sensors and 5 meters is provided in Figure 7 below. The experimental data was fit to a 5<sup>th</sup> order polynomial using non-linear least-squares regression. The coefficients of that fit are provided in eq 5.

The "theoretical" resistivity of water, based on fundamental properties of water, was also re-determined based on the best available literature and it is summarized elsewhere[2,8,9]. A portion of the data and the "theoretical" resistivity of water are also provided in Figure 7.

**Figure 7. Experimental and Theoretical UPW Resistivity Data**



**Figure 8. Experimental vs. Theoretical UPW Resistivity Error**



The relative error between the experimental results and the 5<sup>th</sup> order polynomial fit of the theoretical data is plotted vs. temperature in Figure 8. At this point in time, it is difficult to ascertain whether the increasing error is the result of systematic experimental measurement error or incorrect theoretical data. However, given the large disagreements in

the earlier literature on the value for the conductance of OH<sup>-</sup> at high temperatures, there is high confidence in the experimental methodology. While the most likely culprit may be theoretical conductance of OH<sup>-</sup> at high temperatures, the errors still average less than 1% from literature values.

## Instrumentation

As noted in Table 3, the uncompensated resistivity of ultrapure water is 86 MΩ-cm at 0°C and 1.3 MΩ-cm at 100°C. This requires a resistivity meter/sensor combination with accuracy over nearly 2 orders of magnitude. Furthermore, if verification of the resistivity system is desired in order to utilize ASTM standards, then an additional 2 orders of magnitude range is required. Prior to the initiation of the Thornton studies on the properties of ultrapure water, systems with this performance were not commercially available for this application.

The development of the 770PC instrument provided a measurement system with a dynamic range in excess of 5 orders of magnitude (40 Ω to 10 MΩ), with an accuracy of better than ±0.3% of the measured value across the entire range and typically better than ±0.1%. When used with a variety of sensors that vary in cell constant from 0.01 to 50 cm<sup>-1</sup>, the measurement range of the system extends from 1 nS/cm to 1 S/cm (1000 MΩ-cm to 1 Ω-cm). The availability of these new instruments provides improved accuracy with several orders of magnitude wider dynamic range than previous generations of instrumentation. In addition, the invention of the Smart Sensor™ with embedded non-volatile memory containing precise calibration information for its specific sensor permitted the instrument to continuously monitor the cell constant to 0.01%.

## The Three Temperature UPW Cell Calibration Method

A closed-loop, constant temperature recirculating water system, as described above, is used for this cell constant calibration. The general procedure of the calibration is illustrated in the example below.

The temperature in the recirculating pure water system is set to ~40°C. The temperature is measured by a calibrated, traceable 1000 Ω Pt RTD and a Fluke 8505A ohmmeter. The temperature measurement system is accurate to ~0.02°C. At any temperature, the resistivity of UPW is determined by accurate knowledge of the temperature and from eq (5). For simplicity, suppose the water temperature is 40.00°C. From Table 3, the resistivity of UPW is 8.85 MΩ-cm. If a recently calibrated resistivity meter indicates the resistance<sup>7</sup> to be 0.903 MΩ, uncompensated for temperature, then the cell constant is calculated by:

$$\phi_{40} = \frac{0.903 \text{ M}\Omega}{8.85 \text{ M}\Omega\text{-cm}} = 0.10203 \text{ cm}^{-1} \quad (9)$$

---

<sup>7</sup> Remember that the meter will not display a resistance normally. The displayed value will actually be the calculated resistivity, which is equal to the measured resistance divided by the cell constant. Again, this is all transparent to the user. The alternative way to manually calculate the cell constant is :

$$\text{new cell constant} = \text{old cell constant} \times (\text{measured resistivity} \div \text{reference resistivity})$$

The temperature of the system is then set to ~25°C. The temperature is measured and the resistivity of the UPW is determined from eq (5). Again, for simplicity, let's assume the temperature is exactly 25.00°C. From Table 3, the resistivity of UPW is 18.18 MΩ-cm. If the resistivity meter indicates the resistance to be 1.858 MΩ, then the cell constant is calculated by:

$$\phi_{25} = \frac{1.858 \text{ M}\Omega}{18.18 \text{ M}\Omega \cdot \text{cm}} = 0.10220 \text{ cm}^{-1} \quad (10)$$

The difference between  $\phi_{40}$  and  $\phi_{25}$  is only 0.17%, less than our goal of 0.5%, and therefore acceptable.

The temperature of the system is again lowered, this time to ~15°C. The temperature is measured and the resistivity of the UPW is determined from eq (5). Again, for simplicity, assume the temperature is exactly 15.0°C. If the observed resistance is 3.251 MΩ, then the cell constant is calculated by:

$$\phi_{15} = \frac{3.251 \text{ M}\Omega}{31.75 \text{ M}\Omega \cdot \text{cm}} = 0.10239 \text{ cm}^{-1} \quad (11)$$

The difference between  $\phi_{40}$  and  $\phi_{15}$  is only 0.36% and therefore acceptable.

***If the differences among the calculated cell constants is >0.5%, then the water is impure and/or the cell performance is inadequate over the measurement range. In either case, the calibration is self-checking and erroneous cell constant values will not be accepted.***

The temperatures of 40°, 25° and 15°C are used for example only. Any three temperatures may be used, but the procedure should use sufficiently low and different temperatures to take advantage of the changing sensitivity of the resistivity of UPW and small impurities.

The Three Temperature UPW Cell Calibration Method has been in routine use at Thornton Associates for the calibration of standard reference sensors since 1993. Multiple standard reference sensors are used in its Auto Loop Cell Calibration/Certification System to calibrate production resistivity sensors. These sensors have cell constant accuracies of ±0.5%, and have been deployed by calibration laboratories throughout the world as internal reference standards.

The Production Auto Loop consists of a Neslab heat exchanger to maintain constant temperature, a closed-loop, recirculating water system (PVDF valves, fittings, and insulated pumbing) with multiple sets of nuclear/semiconductor grade mixed-bed ion exchange beds in parallel and series to produce 18.18 MΩ-cm quality water. There are 18 measurement ports for the insertion of production sensors under test and standard reference resistivity sensors and temperature sensors. A sensor under test is never more than 3 positions away from a standard reference cell. Since the calibration is executed at ambient conditions, there is no need to correct for any



temperature gradient across the water system.

Sequential readings from the reference sensors and test sensors are data-logged on a dedicated computer, which records the precise cell constant (determined by the 770PC) for each production sensor and generates a printed certificate of accuracy. *Every production sensor* used for pure water applications is verified and/or calibrated and certified in the Auto Loop as a standard feature and shipped with a Certificate.

A potential future application for the Fundamental Standard will be as a reference to assay stable, high resistivity/low conductivity solutions[11] that can be packaged and made available to verify and calibrate sensors in the field. These solutions will have a resistivity in the pure water range, be stable, and packaged for convenient use, and protected from the impact of airborne ionic contaminants.

## **Cell Constant Lifetime Data**

### **How Long is a Cell Constant Calibration Valid?**

Another question commonly asked is “how long is the cell constant calibration valid?”. Answers vary among the following:

- “you can’t calibrate the sensor” (so ‘how long’ is an irrelevant question)
- “weekly”, “monthly”, or “annually”
- “never”
- “it depends”
- “whenever you (the user) think you need it”

Most of these answers are not very useful, and some of them are not supported with data, but the most honest answer is “it depends”. This vague response can be improved depending on the fluid, the type of sensor, the method of manufacture of the sensor, and the materials of construction. For critical use in semiconductor applications, the fluid is pure water so this is a constant. In this fluid, the use of inert materials such as titanium and PVDF or other fluorocarbon polymers is critical. Titanium forms a naturally-occurring, inert, oxide film on its surface, thus rendering it impervious to de-ionized water. The use of PVDF/fluorocarbons or similar materials is well-substantiated and requires no further discussion. While other materials may suffice, these materials are used in >90% of all resistivity measurements in DI applications.

The concentric cell design, also universally accepted for DI applications, has the advantages described previously. More important, it can be manufactured repeatably and reliably, and it can be calibrated to high precision in a high purity water system such as our Auto Loop Cell Calibration/Certification System. But the question of the lifetime of the calibration is valid. To answer this question, several years ago, when we began our multi-point reference

calibration program, we began archiving the calibration data. Today, we are able to examine the cell constant data of numerous sensors that have been calibrated numerous times in numerous solutions. With this data, we are able to answer the question “how long is the cell constant calibration valid?” for our instrumentation and sensors.

### Lifetime Calibration Data

Every Thornton reference sensor has been calibrated in 5 different solutions : UPW at 3 different temperatures and ASTM D1125-95 Solutions D and C. Specifically, we used UPW at ~10-15°C, 25°C, and 40°C, which correspond to resistivities of ~32, 18, and 9 MΩ-cm. The ASTM solutions produce the resistivity described in Table 5 below. This methodology provided 5 standard "solutions" in which we could determine cell constants across a wide dynamic range, ~700 Ω-cm (ASTM D1125 Solution C) to 40 MΩ-cm (UPW at ~10°C).

**Table 5. ASTM D1125 Solution Preparation Table**

<b>If you want to prepare 1 liter of this solution</b>	<b>Weigh this quantity of KCl (grams)</b>	<b>To get this conductivity (mS/cm) at 25°C*</b>	<b>To get this resistivity (W-cm) at 25°C</b>
A	74.2460	111,342	8.9813
B	7.4365	12,856	77.785
C	0.7440	1408.8	709.82
D	dilute sol'n C	146.93	6806.0

\* Add the conductivity of the dilution water to the final standard value.

The detailed cell constant data over the last 4 years from 13 sensors is summarized in Table 6. This data is for all of our reference standards used in high purity water that had at least four calibration cycles. Data from at least another dozen sensors that have had less than 4 calibration cycles has been omitted for brevity.

Table 6. Cell Constant Calibration Data\*

Cal. Date	Thornton S/N	Cell Constant in UPW at 25°C (~18 MW-cm) (cm <sup>-1</sup> )	Cell Constant in UPW at 10°C (~40 MW-cm) (cm <sup>-1</sup> )	Cell Constant in UPW at 40°C (~10 MW-cm) (cm <sup>-1</sup> )	Cell Constant in Sol'n D at 6.760 kW-cm (cm <sup>-1</sup> )	Cell Constant in Sol'n C at 709.3 W-cm (cm <sup>-1</sup> )
Jan-95	1-14-1	0.1008	0.1008	0.1009	0.1005	0.1000
Dec-95	1-14-1	0.1014	0.1011	0.1015	0.1005	0.1011
Jun-96	1-14-1	0.1005	0.1001	0.1012	0.1006	0.1011
Jan-97	1-14-1	0.1012	0.1014	0.1012	0.1016	0.0987
Dec-94	1-7-1375	0.0991	0.0990	0.0993	0.0980	0.0988
May-95	1-7-1375	0.0994	0.0996	0.0996	0.0987	0.0997
Sep-95	1-7-1375	0.0998	0.0995	0.0996	0.0987	0.0993
Mar-96	1-7-1375	0.1000	0.0996	0.1004	0.0993	0.0995
Oct-96	1-7-1375	0.1006	0.1005	0.1008	0.0989	0.0997
Apr-97	1-7-1375	0.0995	0.0999	0.0998	0.0988	0.0974
Jul-97	1-7-1375	0.0997	0.0992	0.1001	0.0996	0.0981
Dec-97	1-7-1375	0.1000	0.0996	0.0996	0.0990	0.0982
Oct-95	1-7-2139	0.1003	0.0996	0.1005	0.0993	0.1005
Nov-96	1-7-2139	0.1004	0.1001	0.1010	0.0996	0.0992
May-96	1-7-2139	0.1005	0.1004	0.1013	0.1002	0.1002
Jun-97	1-7-2139	0.0999	0.1009	0.0989	0.1002	0.0987
Dec-97	1-7-2139	0.0996	0.0991	0.0993	0.0996	0.0984
Sep-95	1-7-2519	0.0998	0.0994	0.0999	0.0995	0.1001
Mar-96	1-7-2519	0.0997	0.0992	0.1001	0.0997	0.0995
Oct-96	1-7-2519	0.1009	0.1005	0.1016	0.1001	0.1008
Apr-97	1-7-2519	0.0997	0.0999	0.1005	0.1001	0.0987
Jul-97	1-7-2519	0.0997	0.0986	0.1003	0.1010	0.0987
Dec-97	1-7-2519	0.0995	0.0985	0.0996	0.0998	0.0987
Mar-95	1-7-2633	0.0994	0.0995	0.0994	0.0960	0.0988
Dec-95	1-7-2633	0.0998	0.0995	0.0997	0.0986	0.0997
Jun-96	1-7-2633	0.0990	0.0986	0.0994	0.0983	0.0991
Jan-97	1-7-2633	0.0999	0.1010	0.0982	0.0988	0.0969

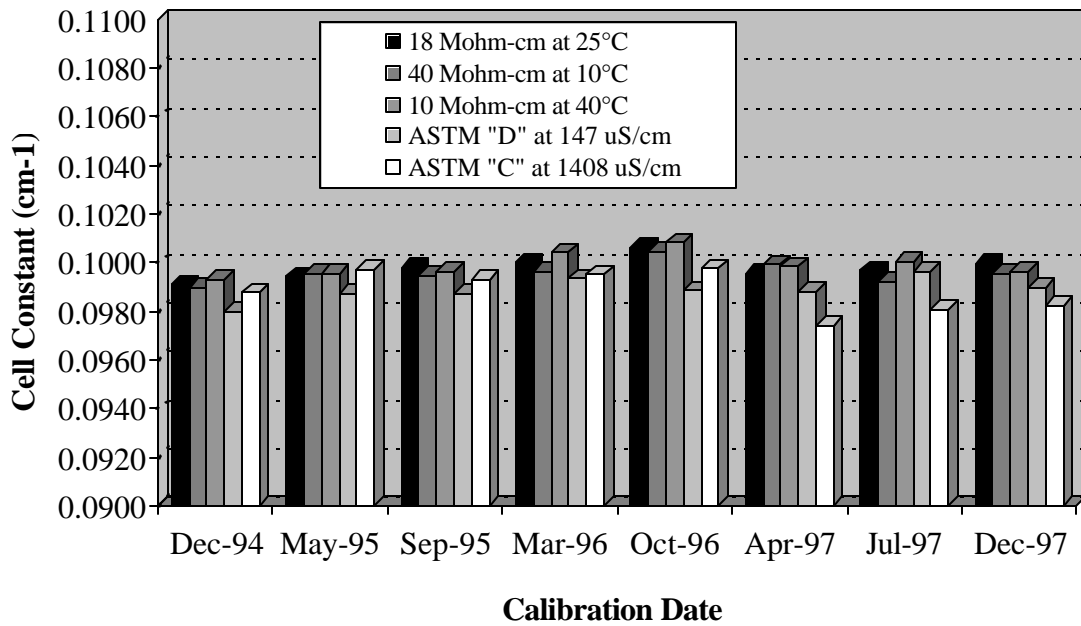
\*The data for solutions C and D include the use of 1 µS/cm water to prepare the solutions.

**Table 6. Cell Constant Calibration Data (continued)\***

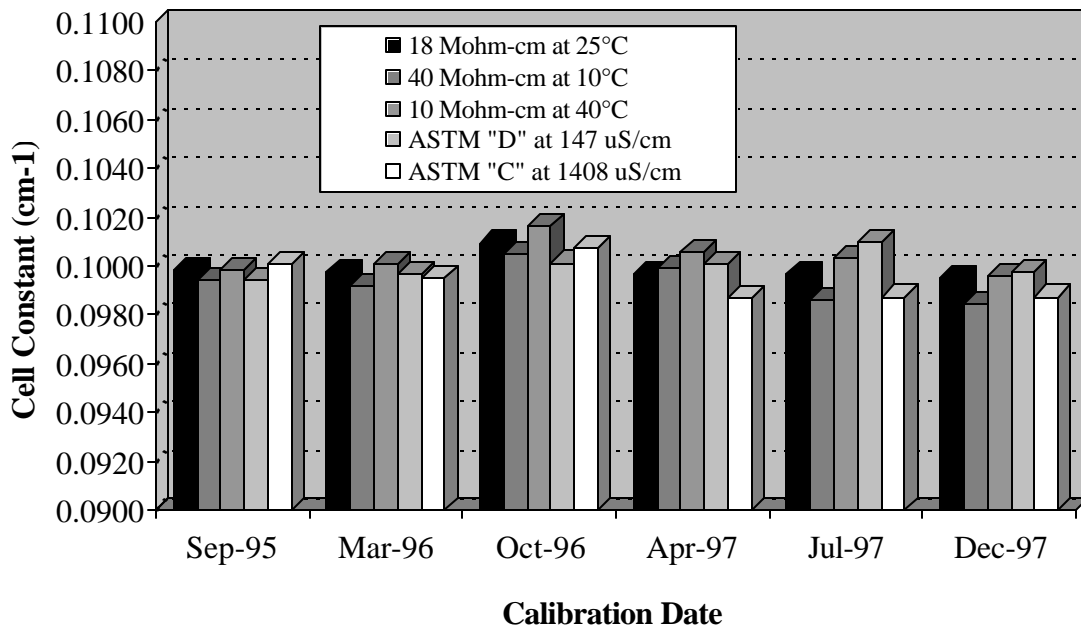
Cal. Date	Thornton S/N	Cell Constant in UPW at 25°C (~18 MW-cm) (cm <sup>-1</sup> )	Cell Constant in UPW at 10°C (~40 MW-cm) (cm <sup>-1</sup> )	Cell Constant in UPW at 40°C (~10 MW-cm) (cm <sup>-1</sup> )	Cell Constant in Sol'n D at 6.760 kW-cm (cm <sup>-1</sup> )	Cell Constant in Sol'n C at 709.3 W-cm (cm <sup>-1</sup> )
Mar-95	1-7-2634	0.0987	0.0987	0.0988	0.0951	0.0982
Oct-95	1-7-2634	0.0990	0.0985	0.0988	0.0981	0.0991
May-96	1-7-2634	0.0995	0.0994	0.0997	0.0989	0.0989
Nov-96	1-7-2634	0.0991	0.0988	0.0996	0.0987	0.0980
Jun-97	1-7-2634	0.0988	0.0992	0.0982	0.0987	0.0970
Dec-97	1-7-2634	0.0983	0.0976	0.0985	0.0987	0.0972
Oct-95	1-7-2635	0.0994	0.0988	0.0992	0.0994	0.0990
May-96	1-7-2635	0.0999	0.0997	0.1002	0.0995	0.0995
Jun-97	1-7-2635	0.0991	0.0992	0.0987	0.0991	0.0980
Nov-96	1-7-2635	0.0997	0.0993	0.1002	0.0993	0.0987
Dec-97	1-7-2635	0.0991	0.0985	0.0988	0.0987	0.0972
Mar-95	1-7-2636	0.0995	0.0995	0.0997	0.0960	0.0990
Dec-95	1-7-2636	0.0997	0.0993	0.0998	0.0986	0.0994
Jun-96	1-7-2636	0.0987	0.0982	0.0994	0.0986	0.0994
Jan-97	1-7-2636	0.0996	0.0993	0.1006	0.0986	0.0967
Dec-94	1-7-349	0.1007	0.0991	0.0994	0.0977	0.0988
Dec-94	1-7-349	0.0990	0.0988	0.0993	0.0981	0.0987
Sep-95	1-7-349	0.0995	0.0992	0.0996	0.0989	0.0999
Mar-96	1-7-349	0.0999	0.0995	0.1001	0.0993	0.1000
Dec-94	1-7-350	0.0993	0.0993	0.0995	0.0983	0.0994
Sep-95	1-7-350	0.0986	0.0983	0.0987	0.1011	0.1001
Mar-96	1-7-350	0.0997	0.0992	0.1002	0.1022	0.1005
Oct-96	1-7-350	0.1007	0.1005	0.1010	0.1014	0.1014
Dec-94	1-7-987	0.0988	0.0980	0.0990	0.0977	0.0988
Mar-95	1-7-987	0.0995	0.0996	0.0997	0.0959	0.0990
Dec-95	1-7-987	0.0997	0.0993	0.0998	0.0987	0.0997
Jun-96	1-7-987	0.0985	0.0979	0.0990	0.0986	0.0991
Jan-97	1-7-987	0.0994	0.0998	0.0989	0.0989	0.0991
Oct-95	1_7_2027	0.0994	0.0991	0.0990	0.0987	0.0996
May-96	1_7_2027	0.1005	0.1005	0.1013	0.1002	0.1001
Nov-96	1_7_2027	0.1001	0.0998	0.1005	0.0989	0.0992
Jun-97	1_7_2027	0.0998	0.1010	0.0986	0.0993	0.0985
Oct-96	208859	0.1000	0.0997	0.1005	0.0990	0.0995
Apr-97	208859	0.1019	0.1017	0.1020	0.1009	0.0997
Jul-97	208859	0.1011	0.1003	0.1017	0.1007	0.0996
Dec-97	208859	0.1006	0.0999	0.1005	0.1014	0.1000

To facilitate understanding this information, data for two of these sensors are provided in Figures 9 and 10. Sensor 1-7-1375 has undergone 8 full calibration cycles and sensor 1-7-2519 has undergone 6 full calibration cycles.

**Figure 9. Lifetime Cell Constant Calibration Data for Thornton Sensor 1-7-1375**



**Figure 10. Lifetime Cell Constant Calibration Data for Thornton Sensor 1-7-2519**



Several features are gleaned from these two figures.

- The small deviations from solution-to-solution and from cycle-to-cycle show that these UPW solutions are as reliable, and probably moreso, than the ASTM solutions; thus UPW would be an excellent resistivity standard solution.
- The determination of cell constant and measurement accuracy is uniform for very high resistivity solutions

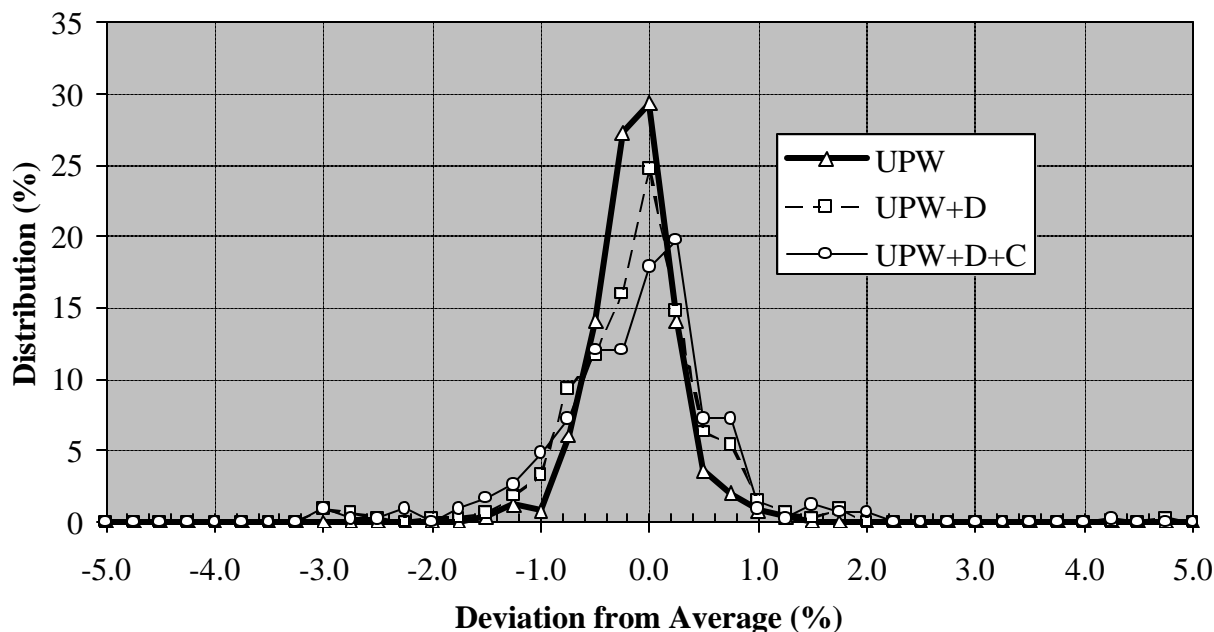
(UPW) and low resistivity ASTM solutions, thus providing the direct evidence for the instrument's wide dynamic range.

- The average cell constant is virtually invariant over at least 2-3 years of operation in UPW, and perhaps longer, depending on the degree of accuracy required.

No data has been omitted from this analysis. The data on Sensors 1-7-1375 and 1-7-2519 is typical of the general performance of all sensors. *The data is consistent with the fact that the cell constant is invariant to the fluid resistivity and that the sensors exhibit little variation over long periods of time.* By contrast, pH sensors may not survive one year in some applications, and they are noted for requiring calibration as often as weekly and daily!

Of further interest is the low variability of the 5 cell constant measurements during each calibration cycle and for every calibration cycle. To get an indication of the accuracy of the calibration method, the distribution of the "relative deviations" for all sensors and all calibrations cycles in all solutions was examined, with no data omitted. A graph of the cell constant distribution as a function of the deviation from the average is shown in Figure 11.

**Figure 11. Statistical Distribution of Cell Constant Calibration Data  
for All Thornton High Purity Reference Standards**



From the distribution plot, we can conclude that the average uncertainty,  $\sigma$ , for all sensors calibrated in all solutions is  $\leq \pm 0.5\%$  (determined from fwhm), and it is less if only UPW calibration data is considered. This further demonstrates the usefulness and reproducibility of using ASTM solutions as reference standards. But more importantly, it provides further evidence that UPW is a reliable, reproducible resistivity standard, and would be a useful fundamental standard.

We have been collecting this cell constant data for a number of years using standard Thornton titanium conductivity/resistivity sensors and 770PC meters. These are commercially-available products whose only difference is that they have undergone numerous calibration measurements. They have been used as R&D tools and been exposed to a wide and uncontrolled variety of fluids ranging from UPW to dilute acids to concentrated salt solutions. They have not received any special or unique treatment.

## **Conclusions**

The resistivity of any pure substance is an inherent physical property. The resistivity of ultrapure water has been accurately established over the temperature range of 0-100°C, yielding a series of reference solutions in the high resistivity range (1.2 to 86 MΩ-cm). These reference solutions, based on the fundamental properties of water, offer many advantages over other techniques for the calibration of resistivity sensors to measure high resistivity fluids:

- Resistivity values are in the proper range and with lower uncertainty than other solutions in this range.
- It is readily prepared at low cost with appropriate equipment.
- It requires no added solutes that must be qualified, dried, and accurately weighed.
- The system described is self-cleaning and the reference solution is not degraded by airborne or atmospheric contaminants, as are batch prepared solutions in open containers.
- The measurement procedure is self-checking and prevents accepting erroneous calibration information.

A pure substance has fundamental physical properties, and it is suggested that the evidence presented here qualifies pure water as a useful fundamental standard for high resistivity, UPW measurements.

Furthermore, the data demonstrates that these sensor's cell constants are traceable, verifiable, and linear using ASTM procedures and standard solutions over at least 4½ orders of magnitude. The resistivity system is demonstrated to be linear and the cell constant is proven to be constant across the crucial measurement range for an UPW system, and the calibration has been demonstrated to be valid over at least 2-3 years.

## **Acknowledgements**

The primary acknowledgements go to the users of resistivity instrumentation. It is they who were asking for high resistivity standards as well as a means to calibrate and verify instrumentation. Their persistence has caused us to develop the lead position in resistivity calibration facilities, and it has caused us to evaluate our sensor capabilities and lifetimes.

Numerous persons at Thornton Associates contributed to the following concepts in this paper: the “3-temperature UPW calibration method”, the “5-point UPW/ASTM calibration method”, the design of the sensor and meter, the concepts and design of the recirculating water loop, accurate temperature measurements, the testing and calibrations,

“UPW as a fundamental standard”, as well as the organizational development of this paper and the recognition of the consumer value/need of this work. Principal collaborators of this work include the following personnel from Thornton Associates :

Anthony Bevilacqua, Ph.D. (Research and Sensor Development Manager)

David M. Gray (Product Manager)

Kenney E. Griffiths (Vice-President of Sales and Marketing)

Truman S. Light, Ph.D. (consultant)

Kenneth R. Morash, Ph.D (Vice-President of Research and Development)

Richard D. Thornton, Ph.D (Professor, MIT Electrical Engineering and founder)

Robert A. Venditti (Director of Instrumentation and Software)

This has been a long-term company-wide effort. Many more persons, not listed here, have contributed to this work. Some portions of this paper have been presented in *Ultrapure Water*[2], at SPWCC last year[1], and at the ESKOM Power Plant Chemistry Conference[12].

## **Background**

Thornton Associates, Inc. has been a leading innovator and manufacturer of sensors and instrumentation to monitor water purity and other fluid-based parameters since 1964, specializing in Ultrapure Water for the semiconductor, pharmaceutical and power generation industries. Thornton instrumentation includes measurements for Resistivity, Conductivity, Temperature, % Acid/Base, Flow, Pressure, Level and more. Thornton continues to be a leader and a technological innovator in the design and development of accurate temperature compensation algorithms, accurate UPW and hot UPW resistivity measurements, patented Smart Sensor™ calibration technology, multi-parameter instrumentation, cell constant reference solutions, and high resistivity applications such as high purity ethylene glycol and isopropyl alcohol cleaning.

## **References**

1. A.C. Bevilacqua, "The Effect of Temperature, Temperature Error, and Impurities on Compensated Conductivity Measurements", *16th Annual Semiconductor Pure Water and Chemical Conference*, pp. 131-160, Santa Clara, California, March 3-6, 1997.
2. K.R. Morash, R.D. Thornton, C.H. Saunders, A.C. Bevilacqua, and T.S. Light, "Measurement of the Resistivity of High-Purity Water at Elevated Temperatures", *Ultrapure Water*, 11(9), pp. 18-26, December, 1994.
3. A.C. Bevilacqua, *Post-Accident Sampling System Owners' Group 14th Meeting*, Philadelphia, PA, September 13-15, 1995.
4. "A New Approach to Accurate Resistivity Measurement of High Purity Water", R.D. Thornton, *Ultrapure Water* (July/August 1989).
5. G. Jones and B.C. Bradshaw, "The Measurement of the Conductance of Electrolytes via Redetermination of Standard KCl Solutions in Absolute Units", *Journal of the American Chemical Society*, **55**, 1780 (1933).
6. "Standard Test Method for Electrical Conductivity and Resistivity of Water", *American Society for Testing and Materials*, D1125-95, 100 Barr Harbor Drive, W. Conshohocken, PA, 19428-2959 (1995).
7. T.S. Light, B. Kingman, and A.C. Bevilacqua, "The Conductivity of Low Concentrations of CO<sub>2</sub> Dissolved in



- Ultrapure Water from 0-100°C", *209th American Chemical Society National Meeting*, Anaheim, CA, April 2-6, 1995.
8. L.E. Strong, "Aqueous Hydrochloric Acid Conductance from 0 to 100°C", *Journal of Chemical Engineering Data*, 25(2), pp. 104-106, (1980).
  9. K.N. Marsh, and R.H. Stokes, "The Conductance of Dilute Aqueous Sodium Hydroxide Solutions from 15°C to 75°C", *Australian Journal of Chemistry*, 17, pp. 740-749, (1964).
  10. "Industrial platinum resistance thermometer sensors", *International Electrotechnical Commission*, IEC Publication 751, First edition, Geneva, Switzerland, 1983.
  11. "Conductivity Cell Standard for Low Ionic Strength Solutions", T.S. Light and R.D. Thornton, *Ultrapure Water* (April 1991).
  12. "Ultrapure Water as a Fundamental Standard for the Calibration of Conductivity/Resistivity Systems", K.E. Griffiths, D.M. Gray, A.C. Bevilacqua, and T.S. Light, "*ESKOM Power Plant Chemistry Conference*", Johannesburg, South Africa, November 25-28, 1997.