MEASUREMENT OF THE RESISTIVITY OF ULTRAPURE WATER AT ELEVATED TEMPERATURES

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Abstract: The use of high temperature ultrapure water (70 to 95°C) has become more prevalent and important over the past few years. This paper examines the special requirements of instruments and sensors for measuring the resistivity of ultrapure water at elevated temperatures.

The resistivity of theoretically pure water over a wide temperature range has been a challenging study for many years. The high sensitivity of resistivity to ionic impurities has been a dominating factor in the widespread use of the resistivity measurement for determining water quality. This sensitivity, however, declines with increasing temperature.

At 25.0°C, pure water has a theoretical resistivity of 18.18 MΩ-cm. If 1.0 µg/L of impurity, calculated as sodium chloride, is added to pure water, the resistivity decreases 3.9% to 17.5 MΩ-cm. However at 100°C, where the resistivity of pure water is 1.29 MΩ-cm, 1.0 µg/L of impurity decreases the resistance only 0.8% to 1.28 MΩ-cm.

To simplify the comparison of solution purity at different temperatures, the industry refers resistivity measurements to a standard temperature of 25.0°C. Modern instrumentation contains sensors for both conductivity and temperature and an algorithm for calculating what the resistivity would be at the standard temperature. This paper will discuss the influence of sensor, instrumental and algorithm variables on the accuracy of ultrapure water measurements at elevated temperature.

The resistivity and conductivity of ultra pure water have been redetermined both theoretically and experimentally and the new data summarized.

Note - Since this paper was presented at the Ultrapure Water Expo on May 10, 1994 the authors have continued to investigate the resistivity of ultrapure water at high temperatures. The additional data collected is included in the analysis in this paper.

Introduction

Henley and others have noted the increasingly important part played by hot deionized water in the manufacture of semiconductors (1-3). The trend, appearing in the last 7 to 8 years, has raised the temperature of the wafer washing water from 40 to 80°C or higher. Some benefits that accrue from the hot water include the inhibition of bacteria growth that is observed at temperatures under 50°C, as well as the usual benefits that come from the use of hot water - increased solubility of impurities and decreased viscosity of water which permits penetration of the smaller spaces created by increased circuit densities.

The modern use of high temperature ultrapure water demands measuring instruments that can detect impurities of only a few tenths of a part per billion (ppb), roughly the same levels that have been measured in the past at lower temperatures (4-7). Unfortunately it is more difficult to measure the purity of hot water than it is to make the same accuracy measurement on cold water. There are a surprisingly large number of sources of error, any one of which can render the measurement inadequate. This paper examines these sources of
error and presents results of new calculations and measurements for the temperature
dependence of the resistivity of water. The focus is on measurement in the range of 60 to
100°C but data is also presented over the range of 0 to 100°C.

Measured Results

In 1989 Thornton and Light (8) conducted a study to calculate and measure the intrinsic
resistivity of ultrapure water from 0 to 100°C. The results showed agreement to values
calculated from other measurements within 0.25% for temperatures below 30°C but
differences rose to almost 3% at temperatures near 100°C. This discrepancy implied that at
elevated temperatures the resistivity change for impurity levels below about 1 microgram per
liter (µg/L or ppb) could not be calculated. Tests performed on several commercially available
resistivity instruments have verified this observation. This is an unacceptable limitation for
modern resistivity instrumentation, so we conducted a new study with detailed attention to
all of the known issues that affect measurement and calculation accuracy. This section
summarizes the measurement phase of the study.

Sources of Measurement Error

The objective was to obtain improved measurements with errors of less than 0.25% over
the entire temperature range. To achieve this level of accuracy we found there were a
number of important sources of error. This section discusses these sources.

Temperature sensitivity of conductivity

Figure 1 shows the importance of accurate temperature measurement. At 0°C the
sensitivity of conductivity (or resistivity) of ultrapure water to temperature is 7.4%/°C.
Therefore an error of 0.1°C in temperature measurement is equivalent to a conductivity error
of 0.74%. At 100°C this sensitivity drops to 2.3%/°C, a factor of three reduction. It might be
inferred from Figure 1 that accurate temperature measurement is less important at high
temperatures, but the issue is more complex than this because the sensitivity of the
measurement to impurity concentration has not been considered.

Figure 1. Sensitivity of pure water conductivity to changes in temperature.
The temperature dependence of the conductivity of the impurity and the sensitivity of the temperature compensation algorithm to temperature errors both have a major effect on temperature compensated conductivity measurements. For the first effect assume that we have NaCl impurities measured in µg/L of NaCl. Figure 2 shows how this sensitivity changes with temperature, and shows a factor of 12 decrease in sensitivity when the temperature increases from 0 to 100°C. Most important, at 25°C the sensitivity is 4%/ppb while at 85°C it is 1%/ppb, so the instrument must be four times as accurate to be as useful at 85°C as it is at 25°C. This means cell constant calibration, instrument and sensor accuracy, and calculation procedures must all be four times as accurate.

![Figure 2. Sensitivity of conductivity change to NaCl impurities as a function of temperature.](image)

The sensitivity of the compensated conductivity to the temperature measurement and to the conductance measurement is shown in Figure 3. A 1°C temperature error at 25°C causes a 4.9% error in compensated conductivity while at 100°C the same temperature error causes a 11.6% error in compensated conductivity. Figure 3 also shows that a 1% resistance measurement error causes about half the percentage error in compensated conductivity as a 1°C temperature error does. Figures 1 and 3 show that as temperature increases a temperature measurement error has less of an effect on the measured resistance but has a greater effect on the compensated conductivity.
Figures 2 and 3 show that at 85°C, temperature must be measured to within 0.1°C and conductivity to better than 1% to get even a rough measurement of impurity with a measurement sensitivity of 1 ppb. The goal of measuring to a few tenths of a ppb is almost beyond the capability of today's instrumentation. Note that at 25°C we only needed to measure to about 3% accuracy to achieve the same instrument accuracy. Thus the temperature measurement only had to be accurate to about 0.5°C. We thus reach the somewhat surprising conclusion that both conductivity and temperature measurement must be more accurate at high temperatures.

Temperature measurement

Typical resistivity cells available today use either a thermistor or Resistance Temperature Detector (RTD) to measure temperature. A thermistor is a semiconductor device whose resistance decreases exponentially with increasing temperature. An RTD is a metal wire whose resistance increases linearly with increasing temperature. Thermistors are generally less precise and more subject to drift than RTDs, but they require less accurate resistance measurement. For the most accurate measurement of temperature it is normally preferable to use a platinum RTD because of its chemical, mechanical and electrical stability.

The platinum RTD has been selected by the National Institute of Standards and Technology (NIST) as the working temperature standard. The accuracy of RTDs has been quantified by the American Society for Testing and Materials (ASTM). The ASTM has defined interchangeability curves for two classes of RTDs (IEC 751 standard). For Class A and Class B 100 ohm platinum RTDs the allowed deviation between measured and actual temperature is:

- **Class A**: $\pm(0.15 + 0.002 [T]) \degree C$
- **Class B**: $\pm(0.30 + 0.005 [T]) \degree C$

Considering only RTD inaccuracy, a Class A 100 ohm Pt RTDs can produce a temperature error of 0.35°C at 100°C even if the resistance is measured perfectly. Individual temperature sensors can be calibrated to provide better accuracy than required by the ASTM interchangeability curves, and the stability of platinum makes such calibration possible. Clearly a Class A platinum RTD or the equivalent is required for the accuracy of temperature measurement required for sensitive impurity determination. In fact, even a Class A RTD must be individually calibrated to achieve the goal of 1 ppb impurity measurement sensitivity.

The measurement of temperature depends not only on the inherent errors in the sensor, but also on errors in the resistance measurement. A platinum RTD has a resistance that
changes about 0.3%/°C change in temperature. An RTD resistance measurement with an accuracy of 0.06% is required to measure temperature to an accuracy of 0.2°C. Since all error sources are cumulative, the actual demands on the instrument are for an accuracy of better than 0.02% in resistance measurement. This accuracy can be achieved by calibration, but only if the measurement has sufficient repeatability in the presence of changes in measurement environment.

For highly accurate temperature measurements a correction must be made for the resistance of the lead wires to the RTD. The use of a 1000 ohm Pt RTD over a 100 ohm RTD will reduce the effect of the lead wire resistance. However, for the most accurate measurements, three or four wire resistance measurements of the RTD should be made.

An additional error factor is the self-heating of the temperature sensor due to measurement currents in the sensor. Very precise resistance measuring instruments can easily cause self-heating of more than 0.1°C, so it may be necessary to sacrifice accuracy for reduced self-heating.

**Conductivity cell calibration**

Most modern conductivity or resistivity instruments either read the cell constant from a smart sensor or allow the user to enter either a cell constant or cell constant correction factor. Unfortunately it is difficult to calibrate a conductivity cell for ultrapure water applications because there is no accepted standard solution that is suitable. A standard must have a resistivity in the same range as the solution being measured or there can be errors from a number of sources; examples include surface effects and measurement frequency and waveform. Well known and accepted standards (9,10) have too low a resistivity. Higher resistivity solutions are generally not stable in the presence of air. Two high resistivity standards close to the desired range have been proposed (11,12) but are not accepted yet.

In our experience the best method of calibrating a resistivity cell is to use ultrapure water. The cell should be initially calibrated in water at 40 to 50°C. It is easy to obtain ultrapure water at this temperature and the sensitivity to impurity is reduced so the calibration can be more accurate. However, calibration depends on knowing the intrinsic resistivity in this temperature range, and there is still some uncertainty that limits the accuracy of high temperature calibration above about 50°C.

The temperature of the water should then be reduced to 25°C where the resistivity of the water is accurately known to be 18.18 Megohm-centimeters (MΩ-cm) on the basis of well-known physical parameters. The cell constant should be verified at 25°C.

The quality of the water can be verified by reducing the temperature and showing that the resistivity increases according to the known temperature relation (see Tables A and B). At the lower temperatures any impurity will have a greater effect on resistivity (see Figure 2) and hence signal the fact that the water was not sufficiently pure to be used for calibration.

**Measurement method**

A prior paper (8) has discussed the importance of using the right electrical frequency and voltage waveform in the measurement. Additionally, since there is a 66:1 change in ultrapure water resistivity between 0 and 100°C it may be necessary to change the measurement frequency and range resistor in the instrument to achieve adequate accuracy over this whole range. The need for accurate resistance measurement for temperature determination has been discussed, but the ac measurement required for resistivity determination tends to be more difficult than the dc measurement of RTD resistance.

**Cleanliness and aging**

Sensor cleanliness is very important. A sensor newly installed in an ultrapure water system must typically operate for several hours before it can be used for reliable measurement. We have observed that there is an initial aging effect that causes the cell constant to change slightly the first time it is used at high temperatures. Once this change has taken place there does not appear to be significant long term drift and the calibration will stay constant for many months.

**Temperature gradient in the cell**

When the cell is measuring high temperature water it is common for the end of the cell furthest removed from the water to be substantially cooler than the water. This temperature
gradient can cause the temperature sensor to be as much as a few tenths of a degree cooler than the water with a resulting temperature error. For successful high temperature measurements it is necessary to use special RTD mounting in the cell and to wrap insulation around the outside of the cell. Cell construction must be such that the temperature sensor is thermally isolated from the cell fitting and cable.

**Thermal time lag**

Sensors for commercial use should be designed to respond rapidly to temperature changes in order to measure compensated resistivity accurately at high temperatures. Fortunately it is possible to design sensors that have a dominant thermal time constant of a small fraction of a minute, so reasonably fast measurements are possible.

**Arithmetic calculations**

With modern microprocessor based measurement it is not hard to perform measurement and compensation calculations with sufficient accuracy, but there are pitfalls to avoid. For example, a simple way to perform temperature compensation is to use table lookup procedures with table values interpolated from data at uniform temperature intervals. The calculation of intrinsic resistivity by this method can lead to unacceptable error at points between table values; hence other methods of interpolation or calculation must be used.

Most conductivity and resistivity instruments now use some method of filtering or averaging. Averaging over long time periods is useful for alarm actuation. However, real time data is often desirable for display purposes. We believe that the best results are obtained with a median filter that excludes occasional extreme measurements but otherwise does not delay the display of changes in measurement more than is necessary.

**Measurement approach**

**Apparatus**

The experimental apparatus has been described previously (8) and some modifications to the measuring equipment have been made to permit the required improvements in accuracy. We used a DI loop with an array of conductivity sensors and a platinum RTD at each end of the array, as shown in Figure 4. At temperatures above 50°C a titanium heat exchanger with a high-powered electric heater was used to heat the water rapidly to the measurement temperature. The water was cooled to a temperature suitable for the resins in the ion exchange purification equipment.

![Figure 4. Schematic of measuring system.](image_url)

In order to measure the temperature accurately we used RTDs at each end of the array of conductivity sensors calibrated to 0.0025°C and were able to interpolate to find the precise temperature of each conductivity cell. The entire loop was wrapped with insulation, but there was still a measurable temperature drop that varied from a few tenths of a degree to about a degree from the first sensor to the last.
High precision resistance measuring equipment was used to measure the RTD resistance and the conductivity sensors. All instruments were accurately calibrated. Repeated measurements at 25°C were used to verify that no changes occurred between successive measurement runs. A resistivity sensor was installed after the cooling heat exchanger to verify the water purity at high temperatures. The water resistivity at this point remained at 18.18 MΩ·cm when the water at the cell bank was at high temperatures thus verifying that the heating was not introducing any impurities into the water.

**Measurement procedure**

After a stable measurement environment was established, we logged all measurements for a substantial time. Computers were used to average the data at each data point for each of the resistivity sensors. Each cell was calibrated to read 18.18 MΩ·cm at 25°C and resistivity was measured to an accuracy of ±0.1%.

**Measurement results**

The data for all sensors was converted into a single determination of resistivity versus temperature. This was done using cubic spline approximating functions with break points at 25°C intervals from 0 to 100°C. The values at the breakpoints were determined by minimizing the mean square deviation of all measurements from the approximating function, and the second derivative at the end points, i.e., 0 and 100°C, were determined so as to minimize the discontinuity in the third derivative at the break points. This method of approximation has been demonstrated to give excellent results when applied to known functions with characteristics similar to the measured data.

The numerical results are given in Table A and the differences between various measured and calculated data are shown in Figure 6. The deviation from the fitted curve for the high temperature data from four cells is shown in Figure 5. The data in Figure 6 is the calculated and observed data from a prior paper by Thornton and Light (8) and new calculations that will be described in the next section.
Table A. Comparison of measured and calculated resistivity.

<table>
<thead>
<tr>
<th>T</th>
<th>$\rho$ measured</th>
<th>$\rho$ calculated</th>
<th>% diff</th>
<th>$\rho$ calculated TL</th>
<th>% diff</th>
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<td>86.07</td>
<td>-0.137</td>
<td>85.90</td>
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<td>-0.521</td>
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<td>35</td>
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<td>4.846</td>
<td>0.120</td>
<td>4.867</td>
<td>0.554</td>
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<td>4.042</td>
<td>4.049</td>
<td>0.176</td>
<td>4.066</td>
<td>0.594</td>
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<td>3.407</td>
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<td>0.245</td>
<td>3.428</td>
<td>0.611</td>
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<td>70</td>
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<td>0.351</td>
<td>2.918</td>
<td>0.763</td>
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<td>75</td>
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<td>2.493</td>
<td>0.455</td>
<td>2.502</td>
<td>0.822</td>
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<td>0.634</td>
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<td>1.877</td>
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<td>1.886</td>
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<td>1.630</td>
<td>1.645</td>
<td>0.946</td>
<td>1.655</td>
<td>1.534</td>
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<tr>
<td>95</td>
<td>1.436</td>
<td>1.451</td>
<td>1.060</td>
<td>1.461</td>
<td>1.706</td>
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<td>100</td>
<td>1.274</td>
<td>1.287</td>
<td>1.024</td>
<td>1.298</td>
<td>1.915</td>
</tr>
</tbody>
</table>

Figure 5. Deviation between measured results and the fitted curve.
Theoretical calculations

Basic equations

Methods of calculating water resistivity from basic principles have been covered in a number of prior papers (8) and only summary results are presented here.

\[
\kappa = \rho^{-1} = \kappa_{\text{H}_2\text{O}} + 10^{-3}(\lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-}) \frac{w}{m_{\text{NaCl}}} \quad \text{Eq. 1}
\]

where:
- \(\kappa\) is the conductivity of pure water with NaCl impurities in S/cm
- \(\rho\) is the resistivity of pure water with NaCl impurities in ohm-cm
- \(\lambda_x\) is the specific conductivity of ion \(x\) in S-cm²/mole
- \(w\) is the impurity concentration in g/liter
- \(m_{\text{NaCl}}\) is the molecular weight of NaCl or 58.45 grams/mole

The conductivity of pure water can be written in a similar way:

\[
\kappa_{\text{H}_2\text{O}} = \rho_{\text{H}_2\text{O}} = 10^{-3}(\lambda_{\text{H}^+} + \lambda_{\text{OH}^-})d\sqrt{K_w} \quad \text{Eq. 2}
\]

where:
- \(d\) is the density of pure water in g/cm³
- \(K_w\) is the dissociation constant of water
Published data

In order to calculate the resistivity of pure water as accurately as possible, we have done an extensive survey and critical evaluation of published measurements of the four physical parameters on the right side of Equation 2. In reviewing the literature we were surprised at the relative scarcity of original data for some of the parameters. In recent years there has been a tendency for researchers to reinterpret past data and fit approximating functions to describe the data. In many cases the approximating functions are fitted for a wide range of conditions and the accuracy is not adequate for our purposes. Thus we chose to take the original data and perform our own interpolation. The conclusions are summarized here for each parameter, and the final values are given in Table B.

Density

The density of water is known to relatively high accuracy. We selected the data prepared by Schmidt (13), which is given for 1°C intervals over the 0 to 374°C range. This data is sufficiently accurate as to not cause even a 0.1% error in the resistivity calculation.

Dissociation constant

There are several recent references with minor differences. Most recent researchers have used data from a 1974 paper by Sweeton, Mesmer and Baes (14). The results agree with other researchers to within about ±0.004 pK units, so errors from this source are estimated to be less than 0.5%.

Specific conductivity of the hydrogen ion

A 1980 publication by Strong (15) is used as the source for specific conductance of the hydrogen ion. His results are relatively recent and the method used appears to be capable of good results. We estimate that the accuracy of this data is about 0.25% at 25°C but the accuracy is less at higher and lower temperatures.

Specific conductivity of the hydroxide ion

The best data for \( \lambda_{\text{OH}^-} \) was found in a 1964 paper by Marsh and Stokes (16). This data was reported for temperatures of 15, 25, 50 and 75°C. Although low temperature data is scarce it is less important because the contribution of the hydroxide ion to conductivity is only half as large as the contribution of the hydrogen ion and the intrinsic conductivity of water is very low to start with. However, at 100°C the OH\(^-\) ion contributes over 40% of the conductivity of pure water and the intrinsic conductivity is larger, so errors are more important. The only data for 100°C appears to be a recomputation of data reported by Noyes in 1907. Marsh and Stokes give a value of 455 Siemens-centimeter squared per mole (S-cm\(^2\)/mole), but others have recomputed Noyes (17) data to arrive at values as low as 427. This is a difficult parameter to measure at high temperatures and we now believe that values inferred from our high temperature water measurements may be the most accurate determination of \( \lambda_{\text{OH}^-} \) to date. We have used the value of \( \lambda_{\text{OH}^-} \) (T=100°C) = 455 S-cm\(^2\)/mole in our calculation and then computed what it should be if our other data is correct.

Calculation results

Tables

The final result of our calculation is shown in Table B and a comparison of our measured and calculated resistivity is shown in Table A.
Table B. Physical parameters and calculated conductivity and resistivity.

<table>
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<tr>
<th>T</th>
<th>$\lambda_{H^+}$</th>
<th>$\lambda_{OH^-}$</th>
<th>$-\log(K_w)$</th>
<th>d</th>
<th>$K_{H_2O}$</th>
<th>$\rho_{H_2O}$</th>
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</table>

Calculated Resistivity

The calculated results given in Table A are plotted in Figure 6 and are compared with previously published data and the results of our measurement. For temperatures from about 5 to 60°C the calculated values of $\rho_{H_2O}$ are estimated to be accurate to about ±0.25% with the probable error rising to more than ±0.5% in the 80 to 100°C range.

The measured and calculated resistivity of pure water as given in Table B can be expressed with an accuracy of ±0.01% by means of the exponential polynomial approximating function in Equation 3.

$$\rho_{H_2O} = e^{a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5}$$

Eq. 3

where: $t = T/100$.

For calculated results use:

\[
\begin{align*}
a_0 &= 4.45518, \quad a_1 = -7.39323, \quad a_2 = 5.48557 \\
a_3 &= -3.74602, \quad a_4 = 1.94396, \quad a_5 = -0.49311
\end{align*}
\]

For measured results use:

\[
\begin{align*}
a_0 &= 4.45666, \quad a_1 = -7.33064, \quad a_2 = 5.02097 \\
a_3 &= -2.56203, \quad a_4 = 0.0643445, \quad a_5 = 0.0140405
\end{align*}
\]
New values for $\lambda_{\text{OH}^-}$

The values for $\lambda_{\text{OH}^-}$ at high temperatures used in this paper were calculated by extrapolating the data of Marsh and Stokes (16) and are therefore not as accurate as desired. New values for $\lambda_{\text{OH}^-}$ at high temperatures can be calculated using the measured $\rho_{\text{H}_2\text{O}}$ from Table A and the values of $\lambda_{\text{H}^+}$, $K_w$ and $d$ from Table B. We report the value of $\lambda_{\text{OH}^-}$ at 75°C to be 373 S·cm²/mole and at 100°C to be 466 S·cm²/mole. These values for $\lambda_{\text{OH}^-}$ are improved based on the higher accuracy of the measured conductivity. The accuracy for determining $\lambda_{\text{OH}^-}$ by this method is limited by the accuracy of $K_w$ and $\lambda_{\text{H}^+}$.

Conclusions

The resistivity and conductivity of ultrapure water have been determined both theoretically and experimentally with particular emphasis on temperatures in the range 50 to 100°C. The theoretical calculations are based on an extensive literature survey for the best original data for the temperature dependence of the density and ion product of water and the specific conductivity of the hydrogen and hydroxide ions. This search showed a paucity of good data on the hydroxide ion at high temperatures and our measurements may allow a more accurate computation than values published in the literature.

Measurement results are given and are believed to be some of the most accurate reported to date. The results are presented in both tabular and equation form suitable for calculation of compensated resistivity. These measurements agree with calculations to about ±0.4% accuracy at temperatures below 70°C but differ by up to 1.0% in the 75 to 100°C range. It is believed that the difference at high temperature is due to both inaccuracies in the available data for the basic physical parameters and the inherent difficulty of making accurate measurements at elevated temperatures.

Sources of error are discussed in some detail and include: accurate calculation of the temperature dependence of resistivity; conductivity cell calibration; measurement method; cleanliness, aging and temperature gradient in the cell; and thermal time lag. Calculations show the sensitivity of the measurement to the error sources, and it is shown that both temperature and resistivity must be measured with much higher accuracy at 75 to 100°C than is necessary at 25°C to achieve the same accuracy in impurity determination. For best results the sensor and instrument must have capability beyond that present in many instruments designed for lower temperature applications. With careful attention to detail it is possible to detect impurities at levels less than 1 ppb at elevated temperatures, but it is significantly more difficult than to make the same determination at low temperatures.

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References