Calibration and Performance of a Conductivity System to Meet USP 23*

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I. Introduction to USP 23

Several years ago, the Water Quality Committee (WQC) surveyed the existing test methods prescribed in USP XXII for the water quality attributes for Purified Water and Water for Injection (WFI), and they determined that the test methods were antiquated, especially considering the current technologies that are available. The mindset of the WQC has been that the "water is not broken", but the testing methods need to be "fixed". For example, the test for the chloride ion, Cl^-, is based on the ability to detect a precipitate or turbidity after $AgNO_3$ is added to the water sample. The inability to detect a precipitate results in the water passing the chloride test. The ability (or inability) to observe microparticles and distinguish them from dust and other ambient particulates results in the potential for operator bias. Furthermore, this type of test results in a "pass" or "fail" status and it offers no information regarding the degree of success or failure. Similar bias-laden methods for ammonia, carbon dioxide, calcium, and sulfate comprised USP XXII.

The WQC, recognizing the limitations of the current methods, knew of the widespread use of conductivity as a total ion monitor for water system maintenance and quality control. Therefore, they siezed the opportunity to upgrade the wet bench test methods :

> *"The existing USP monograph tests for chloride, sulfate, calcium, ammonia, and carbon dioxide were introduced into the USP in 1890 or before and may no longer be appropriate with regard to test methodology. While USP water monograph test methodologies for inorganic ions traditionally have been wet chemical methods, which are inexpensive and require little technical skill to perform, such attributes are offset by the qualitative and subjective nature of the antiquated tests. ...the WQC of PMA proposes to replace them with a conductivity measurement."*[1]

One of the primary achievements of USP 23 has been the replacement of several labor-intensive, qualitative, off-line chemical tests with conductivity measurements for USP Purified Water and WFI. ***USP 23 is in effect on November 15, 1996. There is no "grace" period.*** Conductivity can be applied quickly in-line or off-line, and it is very sensitive to the maximum allowable concentrations (ppb to ppm) of the chemical species of interest. Conductivity is a mature technology which is universally accepted as the preferred methodology to monitor total ion impurities in pure waters.

II. Objectives and Philosophy of Testing Attributes for USP 23

The goals of the USP 23 have been unchanged throughout the process. They are :

- maintain or improve the existing water quality
- improve the reliability of the testing
- simplify the testing (using modern instrumentation)
- reduce the number of tests
- make allowances for in-line testing

To account for the fact that every water system is different, and that the testing facilities and capabilities are not the same at all manufacturing plants, the WQC developed a "3-stage" test plan to allow for 1) the complexities of on-line testing and 2) the innocuous impurities such as CO_2 which directly impact off-line testing. The considerations were the following :

- Permit on-line and off-line testing.
- Set the maximum allowable conductivity to detect the maximum allowable quantity of the ion which produces the lowest conductivity. The maximum allowable quantity is based on conversion of the USP XXII test methods to analytically determined detection limits.
- Eliminate the handicap of using cold water.
- For off-line tests, allow for innocuous contamination that results from CO_2 (HCO_3^- and H^+)
- Eliminate the variations of temperature-compensation methods.

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III. Summary of the Test Method

The conductivity test is a 3 stage method. As soon as one step is passed, the conductivity attribute is passed and further testing is not required for that validation cycle. Here is a summary of the testing.

A. Stage 1 Test

This is primarily intended as an in-line test. Record the temperature and the uncompensated conductivity at the sensors location. If the resistivity is recorded in MΩ-cm, take the reciprocal of the numerical value to get the conductivity value in µS/cm. Round the temperature down to the nearest 5°C and look up the corresponding conductivity value in Table 1. ***If the measured conductivity is lower than the conductivity from Table 1, then the USP Purified Water or WFI has met USP 23 requirements. No further conductivity testing is required.*** If in-line measurements are unavailable, or if the water does not pass the Stage 1 test, proceed to Stage 2 testing.

Table 1. USP 23 Conductivity Limits for Stage 1

Temperature (°C)	Conductivity (mS/cm)	Temperature (°C)	Conductivity (mS/cm)
0	0.6	55	2.1
5	0.8	60	2.2
10	0.9	65	2.4
15	1.0	70	2.5
20	1.1	75	2.7
25	1.3	80	2.7
30	1.4	85	2.7
35	1.5	90	2.7
40	1.7	95	2.9
45	1.8	100	3.1
50	1.9		

B. Stage 2 Test

This is a typically an off-line test. Procure a sample of water from the appropriate location. Store the water sample in an enclosed clean container that has been rinsed previously with water of the same quality. It is preferable to use a Teflon- or plastic-coated vessel to collect and transport the water instead of glass. Pure water is very aggressive to glass and sodium will leach out over time. Adjust the sample's temperature to 25°C and agitate the sample to insure that it has equilibrated with ambient CO_2. Record the conductivity. [Normally, by the time the sample is transported to the laboratory, the sample has equilibrated with the atmosphere.] ***If the conductivity is less than 2.1 mS/cm, then the sample has met USP 23 requirements. No further conductivity testing is required. If the water does not pass the Stage 2 test, proceed to Stage 3.***

C. Stage 3 Test

Take the water sample from the previous test and increase its ionic strength for a pH measurement at 25°C. Record the pH and round it to the nearest 0.1 pH. Look up the corresponding conductivity value measured in Stage 2 above. ***If the measured conductivity is lower than the conductivity from Table 2, then the sample has met USP 23 requirements. No further conductivity testing is required. If the water does not pass the Stage 3 test, the water has failed to meet USP 23 requirements.***

Table 2. USP 23 Conductivity Limits for Stage 3

pH	Conductivity (mS/cm)	pH	Conductivity (mS/cm)
5.0	4.7	6.1	2.4
5.1	4.1	6.2	2.5
5.2	3.6	6.3	2.4
5.3	3.3	6.4	2.3
5.4	3.0	6.5	2.2
5.5	2.8	6.6	2.1
5.6	2.6	6.7	2.6
5.7	2.5	6.8	3.1
5.8	2.4	6.9	3.8
5.9	2.4	7.0	4.6
6.0	2.4		

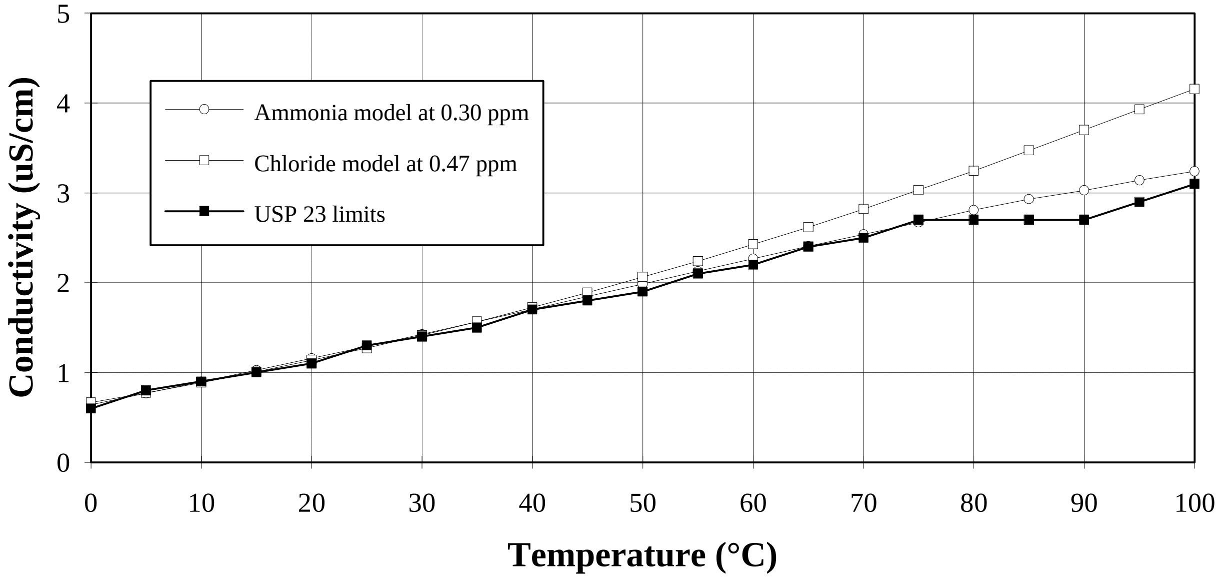
IV. Basis for Conductivity Limits for Each Testing Stage

A. Stage 1 Limits

In the initial stimuli[1], a chemical-conductivity model was established by the WQC to calculate the conductivity at 25°C for chemical systems comprised of the 5 attribute ions in USP XXII. The purpose was to determine the maximum allowable conductivity based on the maximum allowable quantity of the ion which produces the lowest conductivity. At 25°C, the ion producing the lowest conductivity at its concentration limit is Cl^- (0.47 ppm).

However, we expanded the chemical models for each ion to fully account for total charge and mass balance. Upon closer examination and in consultation with the WQC, we determined that the chloride chemical model did not always produce the lowest conductivity as the temperature was varied from 0 to 100°C. We determined that the permissible levels of ammonia (0.30 ppm) and its concomitant ions produce a conductivity that is lower[2] than that produced by Cl^-. A graph of the limiting conductivity for each chemical model as a function of temperature is shown in Figure 1 below. As a result, the WQC has selected a hybrid "chloride-ammonia" model[3] to determine the conductivity limit values for Stage 1 testing. Values for each ammonia model, chloride model, and the USP 23 limits are shown in Figure 1 below.

Figure 1. USP 23 Conductivity Limits for Stage 1



The advantages of on-line conductivity testing have been exploited serving pharmaceutical water systems for many years. A summary of the advantages are :

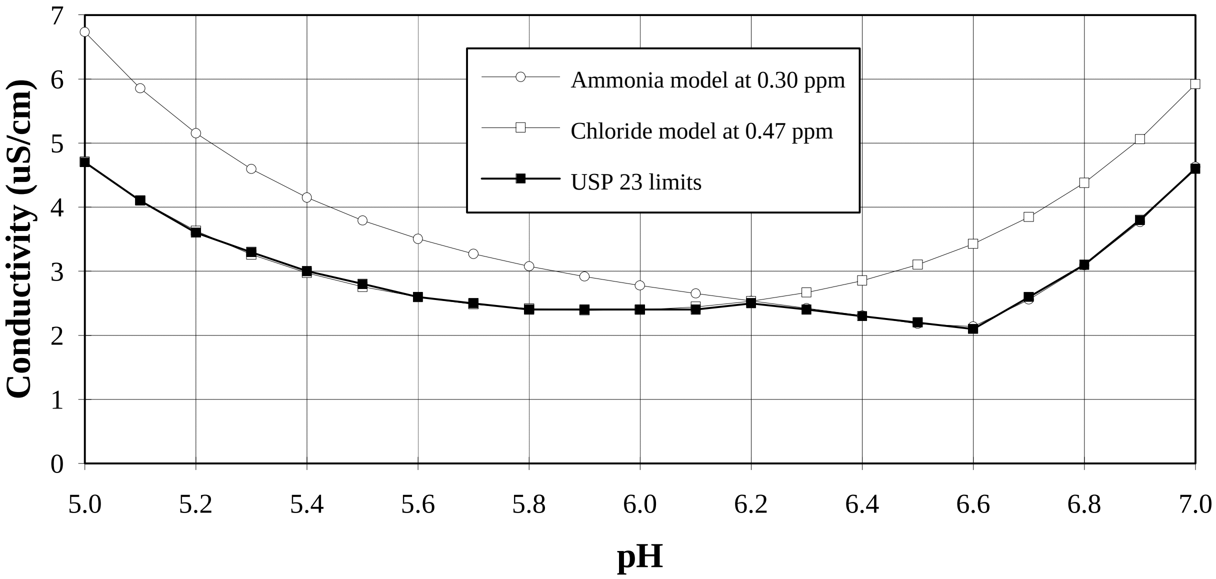
- Real-time conductivity and temperature process information.
- ***Immediate*** alarms and control options.
- Data logging capability to provide a history.
- Easier and cost-effective.
- Eliminate sample collection and transportion errors.
- Temperature-compensated conductivity remains an excellent technique to observe water quality changes, in addition to uncompensated conductivity used for limit detection..

B. Stage 2 and 3 Limits

In pure water systems, the infusion of CO_2 causes an increase in the conductivity (and a decrease in the pH from neutral 7 pH) due to the formation of carbonic acid at concentrations of several hundred ppb. The WQC accounted for this acceptable "impurity" and detemined a minimum conductivity limit for the chloride model with permissible levels of CO_2. In the wake of re-evaluating the models for the Stage 1 testing, we re-evaluated[2] the acceptable conductivity limits for chloride and ammonia based on 300 ppm CO_2 in the ambient. [There is no typical quantity of CO_2 in the ambient. The lowest concentration of CO_2 in pristine air is 350 ppm, while the average upper limit is ~1000 ppm, depending upon the air quality, environment, circulation, and other factors that are difficult to control. This translates to a corresponding increase in conductivity of ~0.8 - 1.5 µS/cm[4]. The chemical model uses a conservative concentration of CO_2, 300 ppm, which causes a ~0.8 µS/cm increase in the conductivity. The choice to use the conservative increase is consistent with the philosophy to set the USP 23 limits based on the minimum conductivity.] The pH is dependent on the quantity of impurity, the form of ammonia, and the the amount of CO_2 in the ambient, thus the calculations of the conductivity limits for the off-line testing (at 25°C) were based on a pH dependence, as well as the different chemistries that are present for chloride and ammonia impurities.

The evaluation of the chloride chemistry and the ammonia chemistry were merged into the "chloride-ammonia" model[3] to account for the fact that the chloride model provides the lowest conductivity below 6.2 pH, and the ammonia chemistry provides the lowest conductivity above 6.2 pH. A graph of the limiting conductivity for each chemical model as a function of pH is shown in Figure 2 below.

Figure 2. USP 23 Conductivity Limits for Stage 3



As a result, the WQC further utilized the hybrid "chloride-ammonia" model to determine the conductivity limit values for Stage 3 testing. Values for the ammonia model, chloride model, and the USP 23 limits at 25°C are shown in Figure 2. The minimum conductivity in the Stage 3 test is 2.1 µS/cm, which is the limit for the Stage 2.

V. Calibration and Performance Requirements

"Calibration features" of instrumentation can be easily overlooked when considering equipment choices. Cost, ease-of-use, and accuracy usually dominate the selection criteria. Today, for numerous reasons, all facets of calibration are very important and ***often critical in the selection process***. This importance was acknowledged by the WQC and confirmed by the USP. In USP 23, there are specific calibration and performance requirements to demonstrate that the conductivity equipment is operating properly.

The calibration and performance requirements are summarized.

- Meter reports uncompensated conductivity or uncompensated resistivity.
- The display resolution is 0.1 µS/cm or better.
- The meter reads accurately to ±0.1 µS/cm when a 0.1% precision resistor replaces the sensor (to calibrate/verify the meter).
- The sensor cell constant is calibrated/verified to ±2%.
- Appropriate dynamic range to meet the above requirements.

A. Uncompensated vs. Temperature-Compensated Display

There was considerable discussion regarding the use of temperature-compensated conductivity values. Early in the revision process, the use of "compensated conductivity" was prescribed. However, the lack of complete understanding of this concept by most users and the inability to properly "verify" compensation calculations ultimately led to its demise. This is discussed in more detail later. Ultimately, it was determined to use uncompensated conductivity measurements at the appropriate 5°C interval. ***Meters that display only compensated conductivity or resistivity do not directly meet the performance requirements of USP 23.***

B. Display Resolution

A display resolution of 0.1 mS/cm is the minimum required. Based on a preponderance of the available product literature, this choice allows the maximum number of instruments and manufacturers to be included. The most versatile instruments have displays with a resolution of 0.01 µS/cm, 0.001 µS/cm, and as low as 0.01 nS/cm. Instruments with a display resolution of 1 µS/cm or more do not meet the performance requirements of USP 23. For meters that display only resistivity, the display resolution is a more complicated value that depends on the operating range. It would have to be at least 0.06 MΩ-cm at the 1.3 µS/cm (0.77 MΩ-cm) limit at 25°C.

C. Meter Accuracy/Calibration

Meters need to be verified that they are "in calibration" within 0.1 mS/cm. Replace the sensor with a precision resistor and calculate the expected response of the meter. For example, wire a precision 100 kΩ resistor in place of the sensor. If the meter is set up to use a 0.5 cm^{-1} constant sensor[5], then the expected response should be

$$100\ \text{k}\Omega \div 0.5\ \text{cm}^{-1} = 200\ \text{k}\Omega\text{-cm} = 0.200\ \text{M}\Omega\text{-cm} = 5.00\mu\text{S/cm}\ .$$

The meter response shall be between 4.9 and 5.1 µS/cm to be "in calibration". ***If the meter response is beyond this range, the meter needs to be re-calibrated.***

D. Sensor Calibration

The sensor cell constant shall be verified to within ±2%. Not all sensors are shipped with an accurately determined cell constant. In fact, it is common to manufacture sensors to a nominal cell constant, but due to tolerances in manufacturing methods, the actual cell constant could be off by ±10% from the stated value. The more advanced conductivity sensors have tolerances as high a 3% and as low as 0.25%. High quality sensors will be provided with accuracy certification that can be used for validation purposes.

The 3 methods that are used to verify and calibrate a conductivity sensor are :

1. Verify/calibrate the sensor vs. another calibrated sensor in the same solution.
2. Verify/calibrate the sensor in a solution with a stated conductivity.
3. Verify/calibrate the sensor in a solution that is prepared to a specific concentration and conductivity.

Each method can be done in the QC lab of any pharmaceutical facility. As an alternative to above procedures, some manufacturers offer calibration services. In that case, the manufacturer should be using one or more of the above methods.

1. *Calibration vs. another calibrated sensor*

Method 1 is the easiest method to perform, ***if you already possess a calibrated sensor***. At some point, a true standard sensor is calibrated in a standard solution, but this section focuses on "transfer" standards. Place the calibrated sensor and the sensor(s) to be calibrated in a beaker or other containment vessel containing a homogeneous mixture of a conductive fluid (water works great!). The conductivity of the fluid should be in the linear response range of the meter and sensor to be calibrated. The sensors should be at the same temperature. It is preferable to place the fluid in a thermostatted bath instead of placing it on the lab bench where it is susceptible to air currents and ambient temperature gradients. Verify that the conductivity of the sensor to be calibrated agrees with the conductivity of the calibrated sensor, within ±2%. If the difference between the two systems exceeds 2%, adjust the cell constant so that the conductivity agrees with the standard within 2%.

2. *Calibration in a solution with a stated conductivity*

Method 2, while it is the most intuitive approach, is the most misunderstood approach. The traditional response is to purchase a "standard conductivity solution" from a chemical supply house. While this appears to be a simple answer to calibration, there are several critical issues that constantly arise with these types of solutions. First, solutions are subject to inhomogeneities due to salt "creep" unless the solution is shaken carefully before use. Second, for very low conductivity solutions, the solution is subject to contamination from the storage container or mishandling. Third, solutions of low conductivity (<100 µS/cm) should be used with reservation. The amount of "contamination" from the ambient air due to CO_2 varies[4], and therefore the proportion of the uncertainty relative to the total conductivity is large. Even NIST solutions (which are probably the most accurately reported) have statistically-based uncertainties in excess of 2% for their 10 and 25 µS/cm standards. Finally, caveat emptor (let the buyer beware), particularly using solutions from commercial catalog houses! After taking all of the necessary precautions and including their stated tolerances, these solutions are not always the conductivity they claim to be.

3. *Calibration in a solution prepared to a specific concentration and conductivity*

Method 3 is the preparation of a solution to a specific concentration using a well-defined procedure. Accurate knowledge of the conductivity of the solution is based on preparation of the solution using volumetric glassware and precision balances. The preferred solutions are based on preparation of KCl solutions according to ASTM D1125-95[6] and the pioneering work of Jones and Bradshaw[7]. These solutions are prepared to very high accuracy when oven-dried, non-hygroscopic, high-purity KCl, Class A volumetric glassware and pipettes, and a balance with 0.1 mg resolution are utilized. A propogation of error analysis results in ~0.03% accuracy based on equipment tolerances. In practice, measurement by conductimetric methods has shown that the error is <0.5%, and that this is the upper limit based on instrument limitations. Gravimetric methods have not been attempted to our knowledge.

The preparation of the different ASTM solutions for sensor calibration is provided in detail in the ASTM Test Method. The quantity of KCl required to prepare Solutions A, B, C and D is provided in the table below[8].

Table 3. ASTM Solution Preparation Table*

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

* Add the conductivity of the dilution water to the value from the table to get the final standard value.

The preference for the ASTM method is based on the definition and the quality of the preparation process. It provides the most reliable and self-assured means of calibration. Some sensors and meters that are designed for use in pharmaceutical waters can not be calibrated in the ASTM solutions because the solution conductivities are beyond the linear dynamic range of the conductivity system. For those systems that cannot measure 146.9 µS/cm (plus the conductivity of the diluting water) accurately, a low conductivity standard is suggested[9].

Another low conductivity standard that can be prepared repeatably and reliably is 18.2 MΩ-cm (0.0550 µS/cm) water[10] at 25°C. In fact, for any temperature from 0-100°C, the conductivity of a pure water system is known precisely[11], making it a fundamental measurement. The process to prepare ultrapure water is well-understood, and ultrapure water lab systems are more prevalent in laboratories today. Therefore, they make excellent "standard solutions" in a closed loop, re-circulating water system with the sensor located immediately following a mixed bed ion-exchange resin. Like above, for those systems that cannot measure ~0.055 µS/cm accurately, another standard is suggested.

E. Sensor Calibration at 1 mS/cm and in Pharmaceutical Waters

The most widely debated issue regarding cell constant calibration is "*if I calibrate at 147 mS/cm or 0.0550 mS/cm, how do I know if my sensor is calibrated at 1 mS/cm?*". Because of the impact of CO_2 on water, there are no standard solutions that can be prepared accurately and precisely in the 1 µS/cm range. Other than trusting the conductivity manufacturer, how do you assure yourself? One valid method that meets all of the technical challenges is to determine the cell constant in pure water and in ASTM solutions. The cell constant is a "geometrical factor" that normalizes the water resistance for the sensor design. The cell constant is a constant over the linear dynamic range of the system. Therefore, if the cell constant is identical at 0.055 µS/cm and 147 µS/cm, then it is the same value at 1 µS/cm. To use a pH analogy, if you calibrate a pH sensor at 4 pH and 7 pH, it may or may not be accurate at 10 pH. However, if you calibrate a pH sensor at 4 pH and 10 pH, it is generally accurate at 7 pH. Although the linearity of the conductivity circuitry is more complex than the circuitry for pH, the same concepts apply.[12]

A track record of measurement rangeability and cell constant consistency has been established for one measuring system. Table 4 shows a series of conductivity sensors that have been repeatedly calibrated in 5 different "solutions" over the last three years : ultra pure water at 3 different temperatures and ASTM D1125-95 solutions "C" and "D". The cell constants were determined by calculating the pure water resistivity based on the temperature which is known to ±0.01°C. The equation relating the temperature (T, °C) and the resistivity (ρ, MΩ-cm) is shown below[11].

$$\rho = e^{(a_0 + a_1 T^1 + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5)}$$

where $a_0 = 4.45656$ $a_1 = -7.33064\times10^{-2}$ $a_2 = 5.02097\times10^{-4}$
$a_3 = -2.56203\times10^{-6}$ $a_4 = 6.43445\times10^{-9}$ $a_5 = 1.40405\times10^{-12}$

The conductivity of the pure water was adjusted from ~0.02 µS/cm to ~0.1 µS/cm (pure water at 15°C to 40°C, respectively). The ASTM solution conductivities were 147.9 and 1409.8 µS/cm, 1.0 µS/cm greater than the values in the Table 3 above, to account for the conductivity of the water.

The "constancy" of the cell constants is displayed in a statistical format in Table 5. The last two columns show the relative standard deviation of the cell constant measurement for all 5 "solutions" (3 pure water and 2 ASTM solutions) and for all solutions except solution C. Note that the relative error is less than 0.5% from 0.02 to 150 µS/cm, across nearly 4 orders of magnitude. The relative error is less than 0.75% from 0.02 to 1400 µS/cm, across nearly 5 orders of magnitude.

F. Temperature Requirements

Temperature requirements for USP 23 are not stated, but there are implicit requirements for in-line conductivity systems. Since you need to know which 5°C interval you are in if you are doing Stage 1 testing, knowledge of the temperature within 0.5°C is a reasonable requirement (one-tenth of the range). Practical, modern instrumentation and sensors will be calibrated to better than 0.25°C. A system using 3- or 4-lead RTD for temperature measurement can support high accuracy in an installation with long cable runs between sensors and instruments.

G. Dynamic Range and Other Requirements

There are no specific requirements for the dynamic range of the conductivity system, but as demonstrated above, the practical requirements are that the conductivity system operate in the pharmaceutical waters (typically 0.2 to 4 µS/cm) and in the fluid that the sensor is calibrated in. This pushes the minimum dynamic range up to ~2-3 orders of magnitude. The "system" includes the instrument, sensor, and cabling since there is a strong dependency on the interaction among the components to achieve good accuracy at the ends of the measurement range.

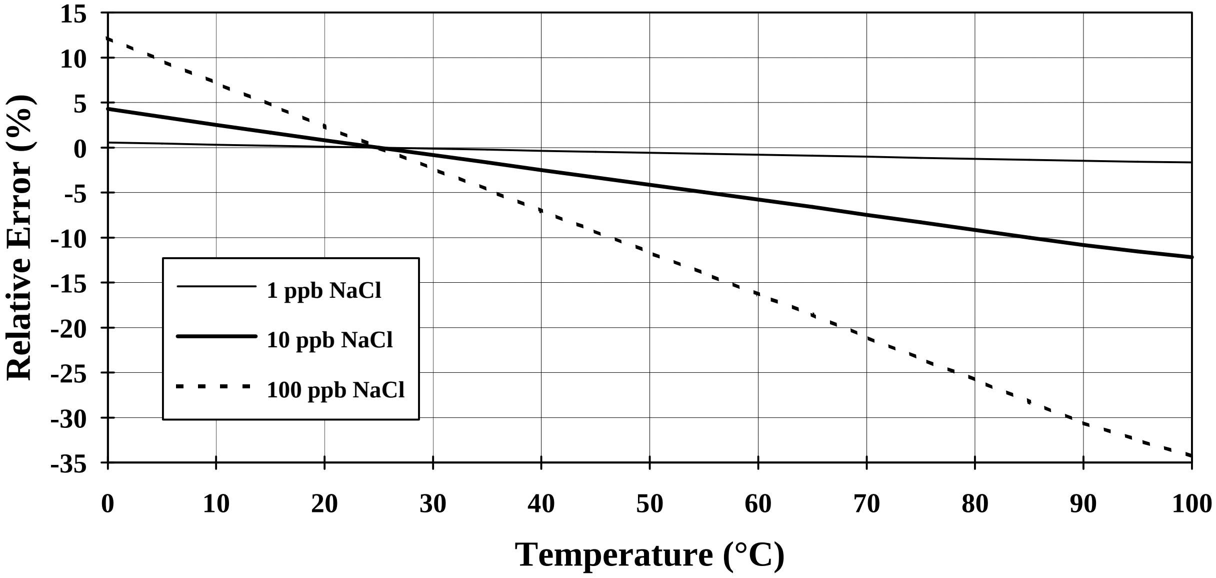
VI. Temperature Compensation, pH, and TOC

A. TemperatureCompensation

A common misconception regarding "temperature-compensated conductivity" (TCC) measurements is that it is a directly-measured physical parameter. In fact, TCC is a processed value that is based on the uncompensated conductivity, the temperature, and the chemical impurity (if there is only one impurity). Often, because the temperature-dependence of most ions is similar (~2.3%/°C to ~1.9%/°C from 0 to 100°C), all neutral salt impurities are categorized together and treated as if they were NaCl. This assumption represents the basis for "standard compensation" that is used in many instruments and is cited in ASTM D1125-95[6].

However, two problems arise with the aforementioned description. First is the assumption that the impurity is a neutral salt. If the impurity is slight acidic or basic, which is very conceivable if there is an air leak or breakthrough at the ion-exchange resins, then the standard compensation calculation is faulty. The temperature dependence of H^+ and OH^-, the ions which dominate under these conditions, is very different from all other ions and thus can give misleading results, particularly at very high temperatures. For example, if an acid impurity is presumed to be the culprit, then it is most appropriate to use "cation[13] compensation". However, if the impurity were really NaCl or most other neutral salts, then inapproporiate temperature-compensation would be applied. Figure 3 shows the effect of using cation compensation at different NaCl concentrations from 0-100°C.

Figure 3. Effect of Inappropriate Compensation Algorithm



The concentrations shown above still represent pure waters, 2 MΩ-cm and higher resistivity. This effect is exacerbated for higher impurity concentrations.

Even if a common impurity could be generally accepted as being the only impurity, the other problem regarding compensation algorithms is that they are very complicated to validate. Because of non-linearity in the conductivity of pure water as a function of temperature and the interdependence of the impurity type and concentration to the dissociation of water, there are virtually an infinite number of temperatures and conductivities that are possible, thereby presenting an overwhelming validation task.

B. pH

USP 23 requires pH testing to assure that the pH is between 5.0 and 7.0 pH. It can be effectively demonstrated that if the water passes the conductivity testing, it also would meet the pH requirements. However, this view was not shared completely, and therefore pH remains an attribute to test. For typical pharmaceutical waters that have been exposed to and equilibrated with air for off-line measurements, the pH will be between 5.3 and 6 pH.

This pH test requirement is separate from the Stage 3 conductivity testing. Although pH is not required for conductivity testing within the first two stages, it is required as a separate attribute and it is perfomed off-line exclusively.

C. Oxidizable Substances Test

The test for oxidizable substances has been modified to permit an optional test, Total Organic Carbon (TOC). The current oxidizable substances test is another wet chemistry test that is based on the appearance/disappearance of color from the addition of permanganate, a powerful oxidizing agent. In the alternative, TOC may be measured instead. This technique is dominated by methods that oxidize carbonaceous materials to CO_2 and detect its presence with conductimetric or spectroscopic methods. The maximum allowable TOC is 500 ppb. The performance requirements state that the TOC system shall have a % recovery of carbon between 85% and 115% with *p*-benzoquinone, after calibration with sucrose, an easy-to-oxidize material. *p*-benzoquinone is an aromatic compound that is the "system suitablity compound", a hard-to-oxidize material. However, any oxidation and detection method is acceptable if it meets the performance requirements.

Although the effective accuracy of the TOC test is ±15%, it is still a better quantitative test than the permanganate test. For an indetermined transitional period of time, either test is acceptable and neither is exclusive. At some point after the transitional period, it is anticipated that the permanganate test will be eliminated and the TOC will be the sole "oxidizable substances" test. The transition period is expected to be at least one year.

VII. References

1. Stimuli to the Revision Process, "Updating Requirements for Pharmaceutical Grades of Water : Conductivity", ***Pharmacopeial Forum***, Nov.-Dec. 1991, pp. 2669-2675.
2. Personal communications : Anthony Bevilacqua to Water Quality Committee, June 1995.
3. In-Process Revision, "<645> Water Conductivity", ***Pharmacopeial Forum***, Vol. 22 (1), Jan.-Feb. 1996, pp. 1844-1849.
4. T.S. Light, B. Kingman, A.C. Bevilacqua, "The Conductivity of Low Concentrations of CO_2 Dissolved in Ultrapure Water from 0-100°C", ***209th American Chemical Society National Meeting***, Anaheim, CA, April 2-6, 1995.
5. On some meters, the exact cell constant can be directly entered by the user. On more advanced meters, the cell constant can be "electronically read" by the meter from RAM located inside the sensor. On many types of older or less sophisticated instrumentation, the instrument is designed to be used with a sensor of a nominal cell constant, with no allowance for cell constant variation.
6. American Society for Testing and Materials D1125-95, "Standard Test Method for Electrical Conductivity and Resistivity of Water", 100 Barr Harbor Drive, W. Conshohocken, PA, 19428-2959.
7. 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).
8. Volumes can be scaled up or down accordingly. Use twice as much KCl to prepare 2 liters of solution. ***Warning : do not scale up or down concentrations***. A solution with ½ the KCl concentration does not have ½ of the conductivity.
9. In some commercial literature, there have been specific references to "Solution E proposed by Thornton and Light to ASTM". This "solution" was based on a 10-fold dilution ASTM D1125 Solution D, but its conductivity was never directly measured or verified by any peer-reviewed process. Furthermore, the concept for a "solution E" was brought to the ASTM D-19 Water Committee in 1991 and it was rejected. *This proposed solution does not meet any of the requirements of a standard solution*.
10. R.D. Thornton and T.S. Light, "A New Approach to Accurate Resistivity Measurement of High Purity Water", ***Ultrapure Water***, July/August 1989.
11. 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***, December, 1994.
12. Although it is commonplace to suggest that the conductivity be near the operating conductivity of the sensor, modern circuit design and internal circuit calibration has overcome that requirement with appropriate calibration methods.
13. This is a common term used in the power industry to monitor water quality. This compensation mode is based on an HCl impurity.

Table 4. Cell Constants in Ultrapure Water and ASTM Solutions "C" and "D"

Date of Calib	Serial Number	Cell Constant in UPW at 25°C (cm^{-1})	Cell Constant in UPW at 15°C (cm^{-1})	Cell Constant in UPW at 40°C (cm^{-1})	Cell Constant in Sol. D at 25°C (cm^{-1})	Cell Constant in Sol. C at 25°C (cm^{-1})
12/12/94	1-14-29	0.09795	0.09759	0.09848	0.09802	0.09797
1/6/95	1-14-29	0.09854	0.09834	0.09877	0.09809	0.09973
12/9/94	1-14-32	0.09996	0.09911	0.09959	0.09684	0.09631
1/6/95	1-14-32	0.09928	0.09905	0.09954	0.09872	0.09883
1/6/95	1-14-1	0.10083	0.10075	0.10093	0.10004	0.10047
12/14/95	1-14-1	0.10144	0.10115	0.10147	0.10110	0.10051
12/9/94	#60	0.12308	0.12205	0.12249	0.12171	0.12091
1/6/95	#60	0.12222	0.12213	0.12226	0.12141	0.12224
12/12/94	1-7-1375	0.09908	0.09897	0.09928	0.09878	0.09798
5/4/95	1-7-1375	0.09944	0.09957	0.09957	0.09972	0.09873
9/15/95	1-7-1375	0.09979	0.09947	0.09964	0.09929	0.09871
3/29/96	1-7-1375	0.10001	0.09964	0.10043	0.09952	0.09933
10/5/95	1-7-2139	0.10032	0.09961	0.10051	0.10053	0.09933
9/15/95	1-7-2519	0.09980	0.09940	0.09986	0.10010	0.09946
3/29/96	1-7-2519	0.09975	0.09920	0.10006	0.09950	0.09969
3/30/95	1-7-2633	0.09940	0.09947	0.09944	0.09882	0.09599
12/14/95	1-7-2633	0.09977	0.09946	0.09967	0.09965	0.09859
3/30/95	1-7-2634	0.09868	0.09869	0.09879	0.09819	0.09505
10/5/95	1-7-2634	0.09898	0.09847	0.09877	0.09909	0.09810
10/5/95	1-7-2635	0.09936	0.09881	0.09922	0.09900	0.09938
3/30/95	1-7-2636	0.09955	0.09952	0.09966	0.09899	0.09596
12/14/95	1-7-2636	0.09973	0.09931	0.09976	0.09937	0.09865
12/9/94	1-7-349	0.10066	0.09907	0.09938	0.09881	0.09765
12/12/94	1-7-349	0.09901	0.09884	0.09932	0.09874	0.09813
9/15/95	1-7-349	0.09953	0.09921	0.09960	0.09986	0.09894
3/29/96	1-7-349	0.09988	0.09946	0.10010	0.10001	0.09929
12/12/94	1-7-350	0.09933	0.09927	0.09954	0.09935	0.09828
9/15/95	1-7-350	0.09864	0.09826	0.09868	0.10010	0.10112
3/29/96	1-7-350	0.09972	0.09925	0.10021	0.10054	0.10218
12/9/94	1-7-987	0.09880	0.09804	0.09903	0.09884	0.09770
3/30/95	1-7-987	0.09952	0.09959	0.09971	0.09895	0.09586
12/14/95	1-7-987	0.09974	0.09933	0.09979	0.09973	0.09874
10/5/95	1-7-2027	0.09936	0.09907	0.09898	0.09959	0.09874

Table 5. Cell Constants Statistics

Date of Calib	**Serial Number**	**Cell Constant Before Recalibration (cm^{-1})**	**Average Cell Constant (cm^{-1})**	**5 point C+D+UPW Relative Std. Dev.**	**4 point D+UPW Relative Std. Dev.**
12/12/94	1-14-29	0.09840	0.09800	0.32359	0.37306
1/6/95	1-14-29	0.09840	0.09869	0.64018	0.29609
12/9/94	1-14-32	0.09728	0.09836	1.69725	1.42391
1/6/95	1-14-32	0.09728	0.09908	0.33459	0.34906
1/6/95	1-14-1	0.10074	0.10061	0.35438	0.40018
12/14/95	1-14-1	0.10074	0.10113	0.38278	0.19178
12/9/94	#60	0.12127	0.12205	0.66937	0.48494
1/6/95	#60	0.12127	0.12205	0.29713	0.32862
12/12/94	1-7-1375	0.09883	0.09882	0.50822	0.21153
5/4/95	1-7-1375	0.09903	0.09941	0.39180	0.11558
9/15/95	1-7-1375	0.09903	0.09938	0.42154	0.21672
3/29/96	1-7-1375	0.09963	0.09978	0.43636	0.41102
10/5/95	1-7-2139	0.09977	0.10006	0.55618	0.43582
9/15/95	1-7-2519	0.09935	0.09972	0.29212	0.28952
3/29/96	1-7-2519	0.09935	0.09964	0.31606	0.36358
3/30/95	1-7-2633	0.09915	0.09862	1.51933	0.31456
12/14/95	1-7-2633	0.09916	0.09943	0.48594	0.13142
3/30/95	1-7-2634	0.09833	0.09788	1.63221	0.27508
10/5/95	1-7-2634	0.09846	0.09868	0.40563	0.27628
10/5/95	1-7-2635	0.09918	0.09915	0.24555	0.24317
3/30/95	1-7-2636	0.09901	0.09873	1.59423	0.30334
12/14/95	1-7-2636	0.09915	0.09936	0.45203	0.23690
12/9/94	1-7-349	0.09925	0.09911	1.09349	0.82778
12/12/94	1-7-349	0.09925	0.09881	0.44354	0.25715
9/15/95	1-7-349	0.09928	0.09943	0.36212	0.27046
3/29/96	1-7-349	0.09945	0.09975	0.35402	0.28222
12/12/94	1-7-350	0.09892	0.09915	0.50319	0.11772
9/15/95	1-7-350	0.09923	0.09936	1.21626	0.81405
3/29/96	1-7-350	0.09930	0.10038	1.11658	0.56474
12/9/94	1-7-987	0.09868	0.09848	0.58694	0.44341
3/30/95	1-7-987	0.09900	0.09872	1.64891	0.33866
12/14/95	1-7-987	0.09917	0.09947	0.45063	0.21605
10/5/95	1-7-2027	0.09903	0.09915	0.33602	0.28085
Average Relative Standard Deviation				**0.669 %**	**0.366 %**