

A Comprehensive Look at Conductivity Measurement in Steam and Power Generation Waters

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ABSTRACT: Conductivity has been the simplest, oldest, most common, most reliable and lowest cost measurement used for determining water purity. Nevertheless, this lowly measurement has provided the means for protecting and assuring efficient operation of billions of dollars worth of power and steam generation equipment throughout the world for over three-quarters of a century. Recent innovations in measurement accuracy, temperature compensation, and sample conditioning have enabled this basic detection method to provide more information and to expand its use even further. From the simplest TDS meter to the most sophisticated ion chromatograph, conductivity measurement is the core technology.

The widespread use of this measurement often outpaces the understanding of it. Provided here are the fundamentals and application of conductivity measurement as used in power and steam generation, including ionic conductance, cell constant, measuring techniques and temperature effects. In addition, various means of sample conditioning are discussed, covering the measurements of cation conductivity, degassed cation conductivity, pH and CO₂ calculations and even TOC (total organic carbon) measurements. It is hoped this discussion will assist those applying conductivity measurement in any of its incarnations to have a greater understanding and to obtain better results.

CONDUCTIVITY THEORY

Conductivity is an intrinsic property of a solution—the ion-facilitated electron flow through it. Electrons will not flow through water by themselves but their charge can be carried by ions. Conductivity is nearly proportional to ionic concentration and is therefore a good indication of water purity. The more ions, the more conductive is the solution. Conductivity will not detect non-ionic materials such as oils or many other organics.

When a voltage is applied to two electrodes immersed in a solution, ions between them will be attracted by their opposite charge and will move toward them to produce a current. To prevent ion migration and electrochemical reactions in the sample, AC voltage is always used for conductivity measurements. The polarity changes frequently enough that ions don't move or react significantly.

Although conductivity is non-specific, responding to all ions, some ions are more conductive than others. Figure 1 illustrates the relative conductances of commonly encountered cations and anions. The much higher conductivity of hydrogen and hydroxide ions makes conductivity much more sensitive to the acids and bases in cation and specific conductivity samples as will be discussed later. It is also the reason that conductivity correlates closely with pH in some samples.

One practice for determining total dissolved solids in low pressure industrial boilers takes into consideration the high conductance of the hydroxide ion in high pH phosphate and/or caustic treatment. The practice takes a grab sample and adds a weak acid such as gallic acid. The acid neutralizes the excess hydroxide conductance without adding much conductance of its own and allows the other ionic content of the sample to be measured without the dominating influence of hydroxide ions.

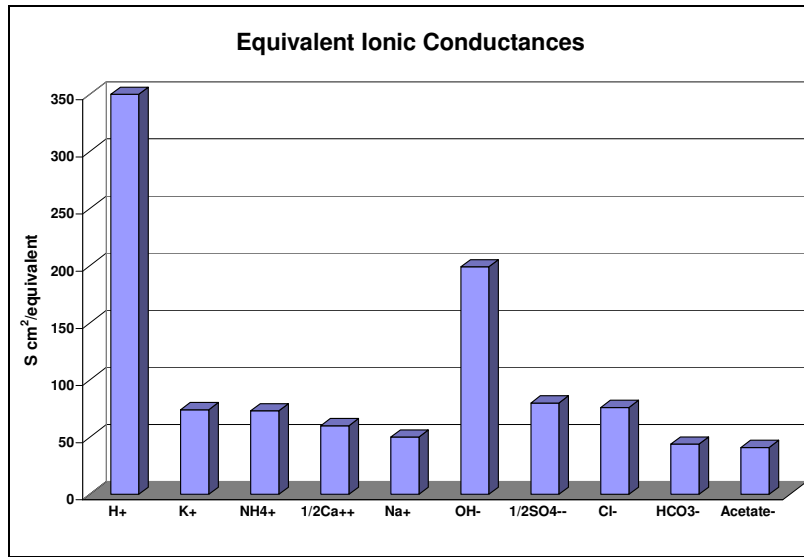


Figure 1 - Conductance of Common Ions at 25 °C

CONDUCTIVITY SENSORS

The size of the electrodes immersed and the spacing between them directly affect the conductance measured. The cell constant is based on the geometry of the two electrodes used to measure the electrical conductance of the fluid. It is the length between electrodes divided by the cross-sectional area of fluid between them, as illustrated in Figure 2a for a 1 cm⁻¹ constant sensor. Lower cell constants (closer spacing, larger cross-section) are needed to provide good signals to the measuring instrument for low conductivity samples. Higher cell constants (wider spacing, small cross-section) are needed to measure high conductivity samples. The measuring instrument must “know” what cell constant is connected and normalize the readout accordingly.

The cell constant has units of cm⁻¹ and results in conductivity having units of

siemens/cm (S/cm). However, some organizations and countries now adhere to strict SI units of siemens/m (S/m) which are 100 times smaller. Further confusion can arise when using micro and milli prefixes when computer font changes or incorrect abbreviation may convert “μ” into “m”. Suffice it to say that considerable vigilance is required in communicating conductivity units accurately.

The accuracy of conductivity measurements is limited by the uncertainty of the cell constant. Most conductivity sensors used parallel plates as in Figure 2a more than 40 years ago. Balsbaugh and Thornton pioneered the now common coaxial conductivity sensor design shown in Figure 2b in the 1960s. It provides the equivalent fixed length/area ratio in a much more robust configuration. Quality equipment suppliers calibrate and certify the precise cell constant of each individual sensor to allow entry of that value into the associated analyzer to normalize the measurement.

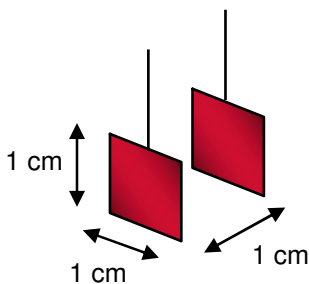


Figure 2a - Cell Constant Derivation

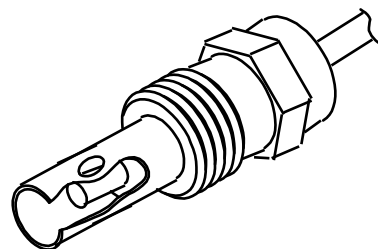


Figure 2b - Coaxial Conductivity Sensor

Ultimate traceability is to ASTM potassium chloride solutions or to NIST Standard Reference Materials.[1,2] Good cases have also been made for using pure water as a standard.[3,4] Precise certification of cell constants involves meticulous work in a standards laboratory and rigorous ISO9001 documented manufacturing procedures with suitable apparatus.

A particularly thorough system for calibrating and certifying cell constants has been developed, with traceability as illustrated in Figure 3. Laboratory standard sensors are repeatedly calibrated in ASTM solutions and then confirmed in a recirculating ultrapure water

loop in the laboratory at three controlled temperatures: 15, 25 and 40°C. Because of the high conductivity temperature coefficient, the three temperatures assure performance at three significantly different conductivity levels in the pure water range: 0.0314, 0.0550 and 0.1130 $\mu\text{S}/\text{cm}$ respectively. These standard sensors are then installed in a temperature controlled recirculating ultrapure water loop in series with production sensors as shown in Figure 4. Both the cell constant and the RTD (resistance temperature detector) temperature compensator are calibrated precisely, in an installation very similar to that of final use in a sample panel.

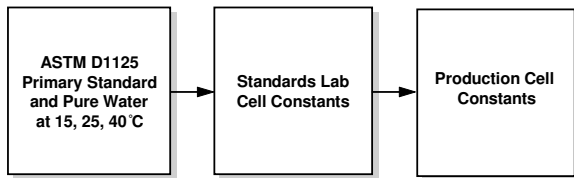
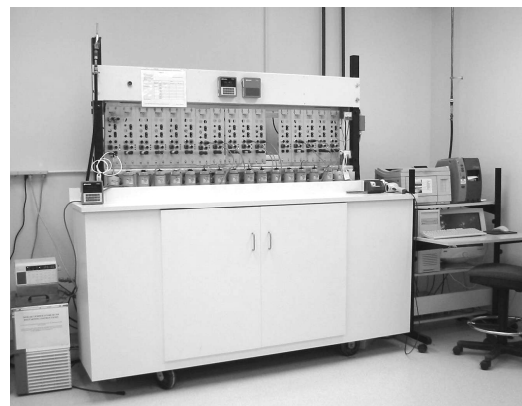


Figure 3 - Cell Constant Traceability

The calibration data is provided either on the cell label, for manual entry into the measuring instrument, or, with a Smart Sensor system, the data is stored in the sensor's memory for automatic reading by the measuring instrument as soon as it is connected. Both methods are provided with certificates of calibration traceable to ASTM.

INSTALLED ACCURACY

Installed accuracy of conductivity equipment requires first that the cell constant and temperature compensator accuracies be precisely certified at the manufacturer's site. But high accuracy must be preserved in an installation even if it involves hundreds of feet separation between sensors and instruments. The AC conductivity signal is vulnerable to leadwire capacitance which increases with cable length. A good conductivity system provides specially shielded cable that works with the



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Figure 4 - Cell Constant and Temperature Compensator Calibration & Certification Facility

measuring circuit to reduce this effect to maintain specifications.

In addition, the modest resistance and temperature coefficient of RTDs makes them vulnerable to leadwire resistance errors. Some systems require temperature calibration after installation. This requires the use of a certified thermometer and a uniform temperature bath, plus the time to reach complete temperature equilibrium for every conductivity sensor—an ordeal at best. Worse yet, this calibration may be ignored, causing conductivity errors as high as 5% of reading per degree C error in the temperature measurement. Well-designed systems handle this through the use of the three-wire RTD measuring technique that compensates for leadwire resistance and eliminates the need for on-site calibration.

Cell constants are quite stable over time in pure waters. However, if a sensor is measuring samples carrying a significant amount of corrosion products, it may be necessary to establish a regular cleaning and

verification procedure. Small volume flow chambers should be used to produce enough flow velocity that particles are carried through the sensor and discharged. If there is some accumulation, sensors should be cleaned with dilute acid on a schedule determined by experience. Sample line filters are not recommended since the filtered particles would accumulate and act as an ion sponge, greatly slowing response downstream.

Cell constant re-verification is also necessary. A convenient on-site procedure is desirable. This can be done using a "plant standard" sensor that is kept clean and used only for such verifications. A comparison can be made using a portable system with the plant standard sensor in a temporary flow chamber piped in series with the sensor being verified. However, the standard sensor itself must be periodically calibrated. It can be returned to the manufacturer for re-certification or verified in-house. Instruments that provide wide range of measurement are most convenient for this.

Some instrumentation has been validated to measure accurately from pure water to well over 147 $\mu\text{S}/\text{cm}$, the lowest of the ASTM standard solutions, with a single cell constant.[5] With such a system, direct calibration is greatly simplified. Despite the gap between the calibration point and the range of measurement, this provides the best accuracy. Standards lower than about 100 $\mu\text{S}/\text{cm}$ have too high an uncertainty (as a percentage of their value) due to variable contamination from carbon dioxide in air as well as the container. This uncertainty would generate much larger errors than those caused by the difference between calibration point and measurement range. Conductivity standard solutions are available from many sources. Care should be taken in selecting and using standards to obtain reliable results.

CONDUCTIVITY APPLICATIONS

Conductivity measurement responds to all ionic contaminants in a sample, whether they are minerals or dissolved gases such as carbon dioxide (in the form of carbonic acid, bicarbonate or carbonate). Contaminants come from many sources. They can be deionizer regenerant chemicals or other materials leaching from inadequately rinsed or fouled resins, air (including CO_2) not completely removed by deaerators, carry-over from drum boilers or leaks from condensers or other heat

exchangers. Conductivity also responds to the treatment chemicals intentionally added.

Specific (direct) conductivity measurement in high pressure boiler cycles is typically dominated by treatment chemicals such as ammonia, phosphates, amines, etc. at ppm concentrations which should be well above the ppb concentrations of any contaminants. Therefore, specific conductivity, often with corroboration by pH, is generally used to monitor and control treatment chemical concentrations.

Cation (acid) conductivity is the technique of continuously conditioning the sample by passing it through a hydrogen form cation exchange cartridge. It enhances the sensitivity to contaminants by two means:

- Ammonia or amines that are intentionally present at ppm levels are removed. This eliminates their high conductivity. The lower ppb concentrations and conductivity of contaminants can then be "seen" by the measurement.
- Contaminant corrosive salts are converted to their respective acids which are typically three times as conductive as the original salt because of the highly conductive hydrogen ion.

This simplicity and detection sensitivity have made cation conductivity the most widely used measure of contamination in the cycle. The upper left of Figure 5 illustrates the specific conductivity sample containing the ammonia and traces of sodium chloride and bicarbonate as typical contaminants. It has a relatively high conductivity due to the amount of ammonia present, represented by the left bar of Figure 6. The conductivity due to sodium chloride (or other contaminants) is almost insignificant. The sample passes through the cation exchanger and the resin "R" retains the ammonia, sodium and any other cations, but always with an excess of resin in the hydrogen form near the outlet. The exiting sample consists of very dilute hydrochloric, carbonic (and other) acids and yields the cation conductivity value represented by the middle bar in Figure 6. A comparison of the two bars shows the enhanced sensitivity for contaminant detection noted above.

Although cation conductivity is widely applied, there has been little standardization of the cation exchange cartridge and this can add many variables to the measurement. In particular, the sample flow velocity through the cartridge must be high enough to promote

turbulent flow and good exchange. If the exchange is not complete, the measurement can be ambiguous. Reasonable guidelines for the

technique have been defined in an ASTM standard.[6]

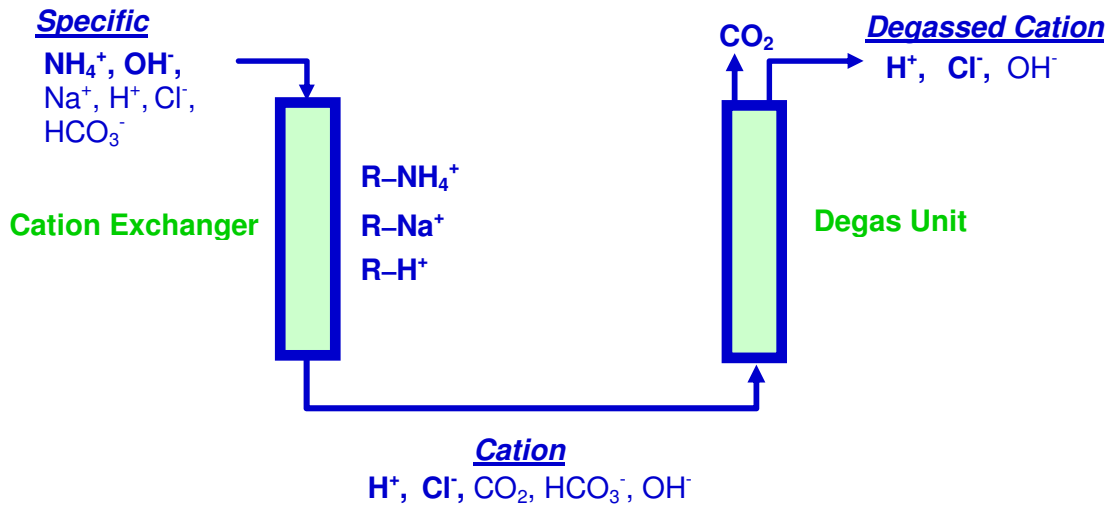


Figure 5 - Specific, Cation and Degassed Cation Conductivity Measurements

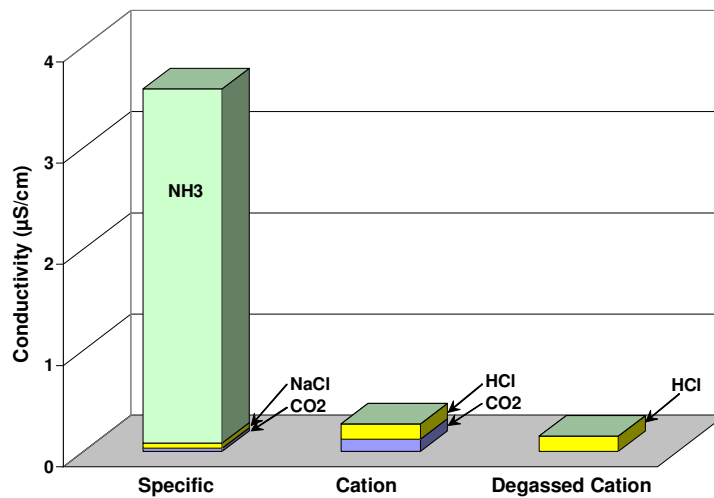


Figure 6 - Typical Specific, Cation and Degassed Cation Conductivity Response

Degassed cation conductivity is useful in plants where carbon dioxide is present in the sample and cation conductivity limits are especially low. A degas unit allows measurement of cation conductivity with the carbon dioxide removed as shown on the right side of Figure 5. Carbon dioxide is acknowledged to be far less corrosive than other contaminants. Degassing can be done with a “reboiler” which heats the sample to boiling to

drive off the carbon dioxide, with a sparging scheme which flows pure nitrogen gas across a thin film of the sample or with a membrane contactor that pulls the carbon dioxide through a membrane. Recent studies have been made on the performance of “reboilers” that showed good results. [7] One evaluation compared performance of reboiler, nitrogen sparger, and membrane systems for carbon dioxide removal and they all performed reasonably well.[8]

Where a reboiler is used and the sample is measured near 100 °C, extremely accurate temperature compensation is required. Some systems re-cool the sample to near 25 °C for this reason. Although not a precise measurement, degassed cation conductivity does serve a very useful purpose.

TEMPERATURE COMPENSATION

Temperature Compensation is required because conductivity is greatly influenced by temperature. All dissolved ions become more mobile and conductive at higher temperatures largely because water becomes less viscous. The increase is at a rate of approximately 2% of conductivity value per °C for most ions. In addition, in pure waters the increasing ionization of the water itself with temperature is significant—there are more hydrogen and hydroxide ions to conduct at higher temperatures. The combination of these two

effects can produce temperature coefficients as high as 5 to 7% of conductivity value per °C. Because of this, guidelines and specifications reference conductivity values to 25 °C which dictates sample temperature control and/or compensation. The relationship is shown in Figure 7, for neutral salt contaminants exemplified by sodium chloride. Conductivity increases with increasing amounts of sodium chloride. However, the temperature coefficient (slope) of the curves increases with decreasing sodium chloride concentration. Also, it can be seen that at conductivity values above 5 µS/cm, the ionization of the water is insignificant and all curves above that are parallel at about 2% per °C. Below that, the non-linearity with both concentration and temperature requires specialized temperature compensation. It should be noted that very few laboratory instruments have more than rudimentary 2% per °C temperature compensation that is unsuitable for low conductivity samples.

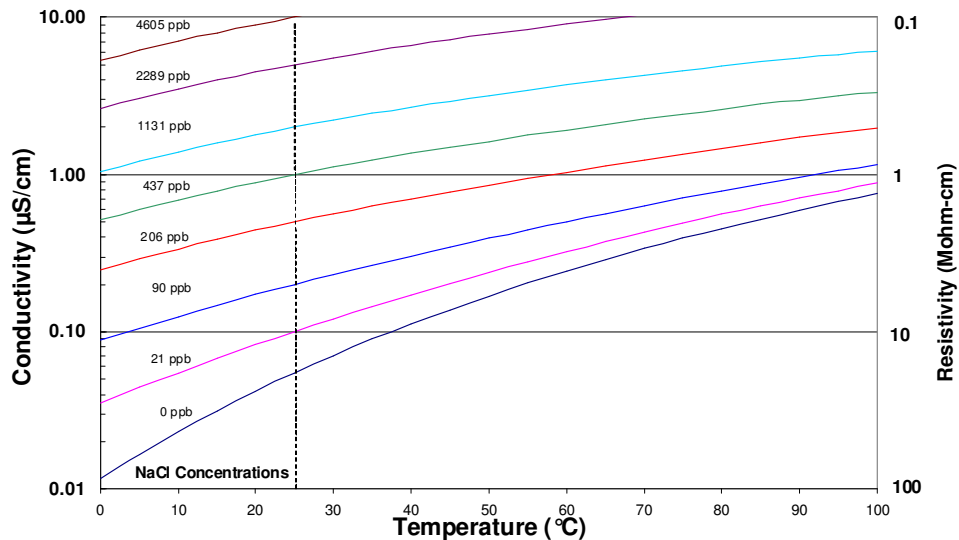
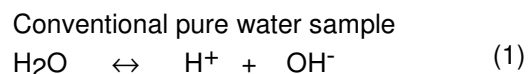
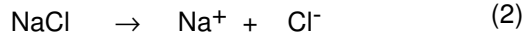


Figure 7 – Figure 7 - Temperature Effects on Pure Water with Neutral Salt Contamination

High purity water compensation has traditionally been recognized as consisting of two separate components: the properties of the pure water and the properties of the impurities in the water. This is appropriate for neutral salt impurities since the ionization of water changes only with temperature, not with dilute salt concentration. Similarly, the mobility of salt ions varies with temperature, independent of the ionization of water. A quick visualization of these effects is given by equations 1 and 2 which take place independently of each other in very dilute

solutions. The combination of these independent effects was quantified decades ago by General Electric for use with nuclear boiling water reactor (BWR) measurements where no treatment chemicals were added. It must be noted that this compensation is appropriate only for BWR samples and for polished makeup water where low levels of neutral salts are the anticipated contaminants.



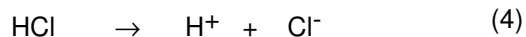
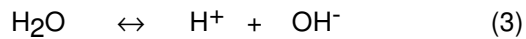


CATION CONDUCTIVITY TEMPERATURE COMPENSATION

Of greatest importance is the temperature compensation accuracy of cation conductivity which has become more critical with the wide acceptance of equilibrium phosphate and oxygenated treatment chemistries. The benefits of both of these treatments depend heavily on maintaining very low cation conductivity levels.

The challenge of pure water temperature compensation is to provide conductivity readout referenced to 25 °C regardless of the actual sample temperature. This can eliminate the cost of expensive and occasionally unreliable secondary sample cooling equipment and can preserve the measurement if a chiller fails.

Cation conductivity sample



A cation conductivity sample behaves differently from makeup water. It has had ammonia and/or amines removed and any salts converted to acids as noted previously. The ionization of acids and water cannot be neatly separated for compensation since they have the hydrogen ion in common. See equations 3 and 4. The additional hydrogen ions from the acid suppress the hydroxide ion of water. This interaction between water and acid ionization and its variation with temperature require an entirely different approach to temperature compensation. The relationship for compensation is much more complex and has pushed the limits of mathematical modeling for a number of years. The standard is to be able to compensate trace hydrochloric acid in pure water across the ranges of concentration and temperature to obtain the value at 25 °C. Hydrochloric acid is representative of cation

conductivity samples because the hydrogen ion has the dominant concentration and the dominant ionic conductance. The anion is of secondary importance. Thus sulfuric, formic, acetic, carbonic and other acids would have essentially the same conductivity temperature characteristics.

The first cation conductivity temperature compensation was developed using the best curve matching that could be developed at that time.[9] In the intervening years, a number of other attempts have been made at providing this compensation but most have failed to achieve reasonable accuracy. A very close curve match to hydrochloric acid in pure water across the full ranges of temperature and concentration was finally developed at Thornton. A comparison of the compensation of several instrument algorithms, with hydrochloric acid data as the reference, is given in Figure 8. A vast improvement was achieved, indicated by the results with Instrument E.[10] It is apparent that temperature compensation is by far the greatest source of error in cation conductivity measurement with most instruments installed in U.S. power plants today.

Temperature compensation algorithms have also been developed for specific conductivity samples dominated by ammonia or amines, and various instruments were evaluated. Similar wide variations in performance were again observed.[11]

While temperature compensation with accurate algorithms can eliminate substantial errors in the measurement, it should be stressed that sample temperature is still important. Since the sample first passes through a cation exchange cartridge, the consistent performance of that exchange is critical. The flow rate and temperature ranges of the sample and the dimensions of the cartridge, as well as the type of resin can all influence cation conductivity results. Note that the cation conductivity temperature compensation algorithm is also appropriate for degassed cation conductivity since carbonic is just one more of the acids that may be present and all have similar temperature effects.

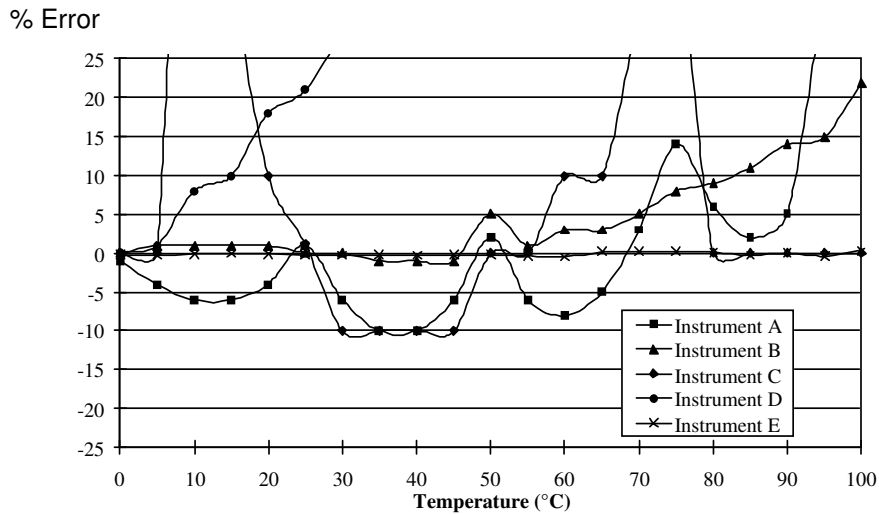


Figure 8 - Cation Conductivity Temperature Compensation Performance at 0.1 $\mu\text{S}/\text{cm}$

PH CALCULATION FROM CONDUCTIVITY

The correlation of pH and conductivity of ammonia has been used for decades to compare cycle chemistry measurements. For a given ammonia concentration in water there is a definite pH and conductivity value which can be calculated from dissociation and conductance data. Because conductivity measurement is typically more reliable than high purity pH measurement, specific conductivity is often used as the primary variable to control ammonia feed although pH is also measured. There are two reasons for conductivity's higher reliability and accuracy:

1. Conductivity is linear with concentration whereas pH is logarithmic. pH therefore has less resolution. For example, a change of only 0.3 pH represents a two-fold (100%) change in both concentration and conductivity in cycle chemistry ranges.
2. pH reference electrode junction potential is notoriously less stable in low conductivity samples and that instability is frequently greater than ± 0.1 pH, depending on the electrode system used.

Inherent in the simple correlation above is the assumption that there is nothing else present but ammonia and water. Any traces of carbon dioxide and/or mineral contaminants must be negligible. Under many operating conditions, this is a reasonable assumption. However, as these trace contaminants grow in concentration during plant startup, unusual

conditions, or upsets, their effects must be accommodated.

Refinement of the conductivity and pH correlation has been accomplished in various ways by several organizations and was discussed previously.[12] Specific conductivity is the primary influence while cation conductivity is used to trim for the presence of small amounts of mineral and/or carbon dioxide contamination. These algorithms still assume that the primary specific conductivity (and pH) influence is ammonia or amines and that the contaminants have lower concentrations. Generally, the pH must be within 7.5-10.5 and specific conductivity must be greater than cation conductivity, especially at low conductivity levels.

Specific conductivity is dominated by hydroxide and ammonium (or amine cation) which are at the highest concentrations. Hydroxide ion conductivity is 3 times that of other ions (except hydrogen, which is suppressed at the high sample pH). Cation conductivity is dominated by the hydrogen ion which is about 7 times as conductive as other ions (except hydroxide, which has a suppressed concentration at the low pH in the sample at this point) so it makes little difference just what the mix of anions is among chlorides, bicarbonates, sulfates, or others.

pH calculation algorithms provide very accurate determinations when the sample composition complies with the conditions above. This excellent performance is acknowledged by its use in plants around the world, especially in Europe. However, it is also important to be aware of the errors that can be produced when

operation goes well outside normal operating conditions.

To eliminate this risk, multi-channel, multi-parameter instrumentation can measure specific and cation conductivities, compute pH from them, and simultaneously measure from a pH electrode as shown in Figure 9. This kind of instrumentation covers both situations: it provides highly accurate calculated pH measurement under normal conditions and can give a warning based on a pH electrode measurement when conditions become abnormal.

The multi-parameter instrument can also display and alarm on the difference between the calculated and the measured pH values. This kind of diagnostic can identify the need for pH electrode maintenance or calibration, or warn of

conditions outside the range for accurate pH calculation as well as conditions exceeding cycle chemistry guidelines.

The availability of both calculated and electrode pH measurements allows more accurate calibration of the electrode measurement when operation is within the conditions for accurate computation of pH. The electrode system should previously have been calibrated at two points using buffer solutions to set up the span response. The final one-point trim calibration eliminates variations in electrode diaphragm/junction potential in buffer solutions and can easily be done more frequently. It greatly enhances the accuracy, reliability and diagnostic capability of the electrode measurement, as well as saving considerable time.

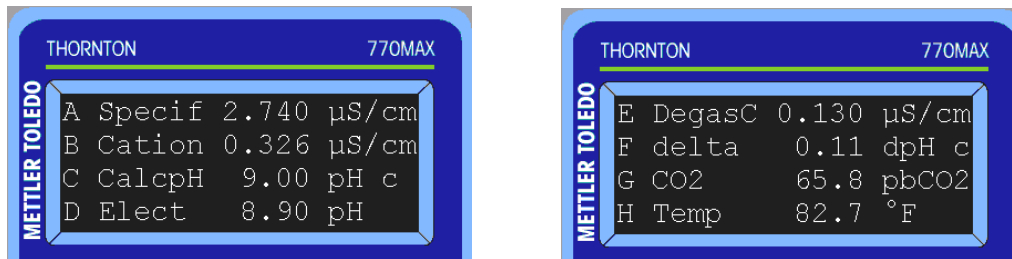


Figure 9 - Two pages of the display of a multi-parameter instrument configured with sensors for Specific, Cation and Degassed Cation Conductivity plus a direct pH electrode

CALCULATED CARBON DIOXIDE & ANIONS FROM CONDUCTIVITY

As noted previously, plants may have carbon dioxide present in steam and condensate samples and it is worthwhile to distinguish it from more corrosive contributors to the cation conductivity. Degassed cation conductivity provides this. Taken a step further, carbon dioxide concentration can be inferred from the difference between cation conductivity and degassed cation conductivity.[13] Again, multiparameter instrumentation can combine the measurements by interpolating ASTM standard tables in its memory to provide display and output signals for carbon dioxide as shown in the second screen of Figure 9.

Yet another parameter that can be obtained is the anion concentration in the degassed cation conductivity sample. If the conductivity at that point is assumed to be all due to chlorides or sulfates, a conversion to concentration can be done. The same instrumentation including ASTM conversion

tables in memory easily makes the conversion to display, alarm and output ppb concentrations of chlorides or sulfates.

TOTAL ORGANIC CARBON FROM CONDUCTIVITY

Most organics are nonconductive and cannot be sensed by conductivity alone. Nevertheless, organics frequently foul resins and can be corrosive and need therefore to be detected and removed. The simplest method for TOC (total organic carbon) detection is based on high intensity ultraviolet oxidation of a continuously flowing sample. Organics are oxidized to carbon dioxide. Conductivity measurements are made both upstream and downstream of the UV lamp. The first measurement accounts for any conductive contaminants already in the sample while the second measurement detects the increased conductivity due to added carbon dioxide. The conductivity measurements and their difference

are compared using a correlation curve to produce a consistent TOC measurement.

Figure 10 shows the flow path of this kind of TOC sensor. Oxidation takes place in a quartz coil surrounding the high intensity UV lamp. It can be seen that the sample flows continuously and there are no solenoid valves, moving parts, membranes or reagents. Response time is particularly fast, taking less than 60 seconds for the sample to pass from the inlet to the final conductivity sensor. The simple design reduces maintenance to simple replacement of the UV lamp on an annual basis.

This technology does have application limitations. It is used only on pure water samples with conductivity $\leq 2 \mu\text{S/cm}$ and TOC of 0.05 - 1000 ppb. Also, alkalinity should be much less

than the TOC concentration since the carbon dioxide oxidation product would otherwise be neutralized by alkaline materials and would not produce the expected increase in conductivity. For these reasons this technology has been recommended primarily for the clean end of makeup water treatment systems.[14] However, more recent evaluations on ammonia-treated cycle chemistry samples measuring after a cation exchange cartridge show promising results with a direct conductivity TOC sensor. Clean cation resin allows organics to pass through and lowers the pH and conductivity to a range where this TOC measurement technique excels. This type of TOC sensor is also available for use with the multiparameter instrumentation previously noted.

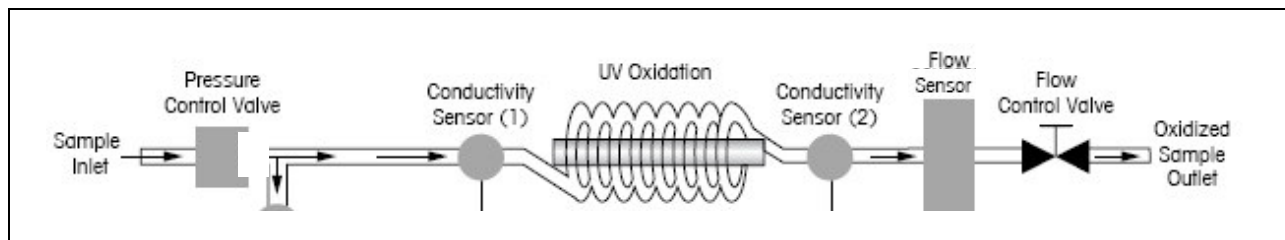


Figure 10 – Flow path of a direct conductivity TOC sensor

CONCLUSION

In the past, conductivity measurements have been viewed as only trend indicators to detect major changes in operating conditions. Today, there is more understanding of long term corrosion mechanisms. Observing the absolute conductivity limits of the applicable EPRI or ASME guidelines and turbine manufacturer specifications over long-term operation can be

as significant to plant equipment reliability and life as the detection and correction of upset conditions. Accurate application-specific conductivity temperature compensation has greatly aided these improvements. A number of sample conditioning techniques plus multi-parameter instrumentation allow conductivity measurements to obtain even more specific information about contaminants.

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