

**PRACTICAL APPLICATION OF SPECIFIC AND
CATION CONDUCTIVITY MEASUREMENT**

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INTRODUCTION

The basics of conductivity measurements used in steam power plants are reviewed and common pitfalls are examined with examples from actual installations. State of the art instrumentation and techniques can provide more consistent results and improve the confidence in these key measurements. Coverage includes the basics of cell constant, calibration, instrumentation, temperature measurement and compensation, and cation conductivity standardization and performance.

The importance of conductivity measurements is reflected in new cycle chemistry guidelines and the emphasis being given them. Newer chemistries such as oxygenated treatment, all-volatile treatment and equilibrium phosphate treatment depend more heavily on reliable and accurate low cation conductivity measurements for their success. Once-through boilers, in which boiler blowdown does not exist, also tend to increase dependence upon on-line measurements since any contaminants which exist in the feedwater are either deposited on heat transfer surfaces or passed on to the turbine. Either situation has serious impact on the reliability and efficiency of the plant since corrosion related failures or reduction in operating efficiency will occur. Where conductivity used to be monitored only for trends to identify significant leaks or other contamination, now there is more emphasis on its absolute value.

At the same time, improvements in instrumentation and its application can bring increased confidence in making decisions based on measured values. As operators and chemists have fewer false alarms caused by sensor failures, sampling system temperature excursions, and other events not related to the actual cycle conditions, they will take real conductivity upsets more seriously.

CELL CONSTANT CALIBRATION

The accuracy of conductivity measurements is dependent on knowing the exact cell constant. Quality equipment suppliers determine and certify the precise constant of each individual cell to allow use of that value by the associated analyzer. Ultimate traceability is to ASTM D1125 solutions or to NIST Standard Reference Materials.^{1,2} Precise certification of cell constants involves meticulous work in a standards laboratory and rigorous ISO9001 documented manufacturing procedures with suitable apparatus.

Factory Calibration

A particularly thorough system for calibrating and certifying cell constants has been developed, with traceability as illustrated in Figure 1. Laboratory standard cells 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 cells are then installed in a temperature controlled recirculating ultrapure water loop, in series with production cells, as shown in Figure 2. Both the cell constant and the RTD (resistance temperature detector) temperature compensator are calibrated precisely, under conditions very similar to those of final use.³

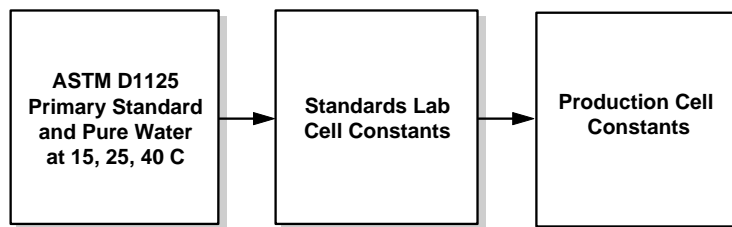


Figure 1 - Cell Constant Traceability



Figure 2 - Cell Constant Calibration/Certification System (Thornton Inc.)

The calibration data is provided either on the cell label, for manual entry into the measuring instrument; or with a Smart Sensor system, stored in the sensor's non-volatile

memory for automatic reading by the measuring instrument as soon as it is connected. Both methods are provided with certificates of calibration traceable to the ASTM standard.

Factory instrument calibration is performed with NIST-traceable standards and is documented with a certificates calibration.

On-site Calibration

For conductivity systems that have been installed for extended periods, especially if corrosion products accumulate from the sample, it is good practice to periodically verify their measurements and re-calibrate if necessary. This is normally done in two steps: one for the instrument and one for the system including the sensor.

The instrument is verified by installing a precise resistance at the input for the cell and another for the temperature compensator, to simulate measurements in the range of interest. Observe the readout and compare with expected values. For especially convenient checking, manufacturers may offer calibration modules containing NIST-traceable resistances that can be plugged into the input cable in place of the sensors. Otherwise, a precision resistance decade box must be temporarily wired to the input. The resistance for simulation must take into account the cell constant setting in the instrument as follows:

$$\text{Resistance (Mohms)} = \text{cell constant (1/cm)} / \text{conductivity } (\mu\text{S/cm})$$

The resistance for the temperature compensator depends on the type of RTD or thermistor used. If temperature compensation is active, the temperature must be simulated at exactly 25°C to eliminate its effect on the conductivity reading.

Cell constants are quite stable over time in pure waters. However, if a cell is measuring samples carrying a significant amount of corrosion products, it may be necessary to establish a regular cleaning and verification procedure. Some of this can be avoided if small volume flow chambers are used to produce enough flow velocity that particles are carried through the cell and discharged. If there is some accumulation, cells should be cleaned with dilute acid and/or ultrasonic bath on a schedule determined by experience. Sample line filters are not recommended since filtered particles would accumulate and act as an ion sponge, absorbing and releasing ions, and greatly slowing response downstream.

The sensor and system are usually verified by comparison with a portable system that has been calibrated in the lab to ASTM standards or has been returned recently to the manufacturer for re-calibration. The portable sensor/flow chamber is connected in series with the sample from the on-line sensor/flow chamber and readings compared. Calibration may be needed. The two systems should have identical temperature compensation algorithms active to account for any minor temperature change that occurs between sensors. It is important to recognize that most laboratory conductivity instruments do not have proper high purity temperature compensation and none have compensation suitable for cation conductivity samples. Therefore an on-line type instrument should be used as the portable.

The standard cell 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. A measuring system 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.³ This is produced by a measuring system with internal auto-ranging that automatically adjusts applied voltage and frequency to obtain optimal response, avoiding both electrode polarization and leadwire capacitance errors.

With such a system, direct cell calibration is greatly simplified. Despite the gap between the calibration point and the range of measurement, this provides the best accuracy. Typical use of standards lower than about 100 $\mu\text{S}/\text{cm}$ yields too high an uncertainty (as a percentage of their value) due to variable contribution from the carbon dioxide in air as well as other contaminants. This uncertainty would generate much larger errors than those caused by the difference between calibration point and measurement range.

INSTALLED ACCURACY

Although the cell and temperature compensator accuracies are certified by the manufacturer, these must be preserved in an installation that may involve long wiring distances 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 measuring circuit to reduce capacitance effects and thereby maintain accuracy specifications even with long wiring distances. It is critical to adhere to manufacturers' length and wire-type 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 cell. If this calibration is ignored or done poorly, conductivity errors of 4 to 6 % of reading per degree C error in the temperature measurement can result. Improved systems handle this through the use of pre-calibrated sensors and a three or four-wire RTD measuring technique that eliminates leadwire resistance effects and the need for on-site calibration.

TEMPERATURE COMPENSATION

After discussing the basic conductivity and temperature measurement concerns, it is appropriate to address the combination of the two: temperature compensation. Of greatest importance is the temperature compensation accuracy of cation conductivity which has become more critical, as discussed previously. The benefits of these treatments depend heavily on maintaining very low cation conductivity levels.

Pure Water Temperature Compensation

The challenge of pure water temperature compensation is to provide a conductivity readout referenced to 25°C regardless of the actual sample temperature. This can eliminate the cost of expensive and often unreliable secondary sample cooling and can preserve the measurement if a chiller fails. This need for specialized pure water temperature compensation can be appreciated from Figure 3.

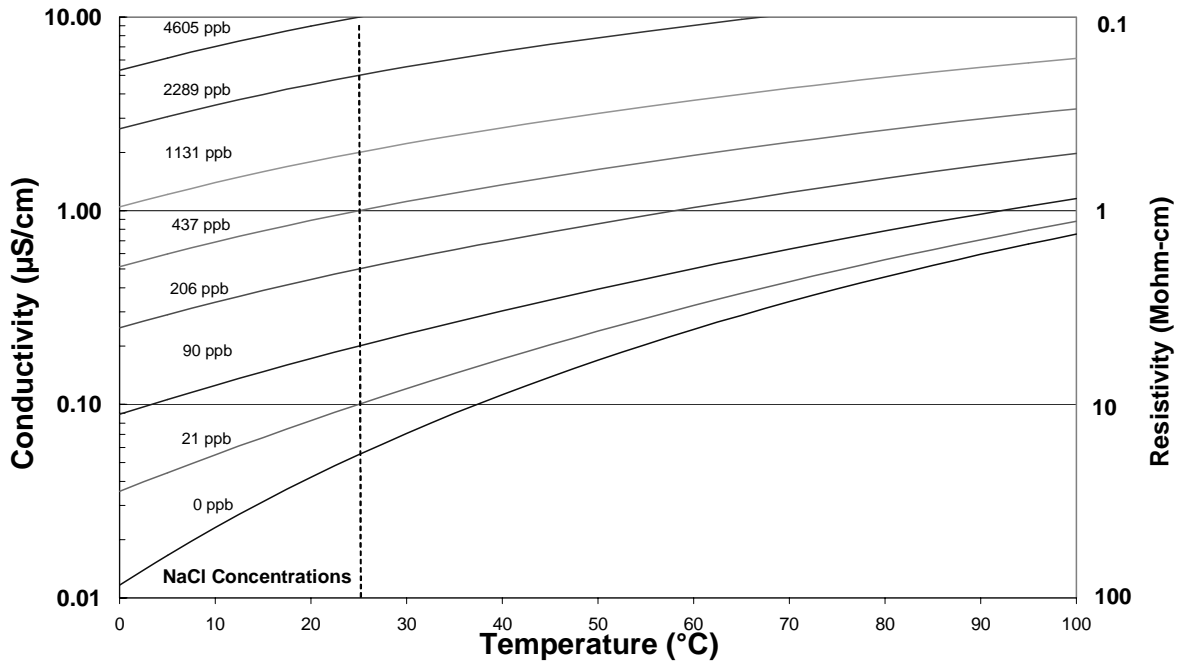


Figure 3 - Temperature/Conductivity Characteristics of Pure Waters

High purity water conductivity temperature compensation has traditionally been acknowledged 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. The combination of these independent effects was quantified decades ago by General Electric for use in compensating boiling water reactor (BWR) measurements where no treatment chemicals were added. It must be noted that that this relatively simple compensation is appropriate only for BWR samples and for polished makeup water where neutral salts are the anticipated contaminants.

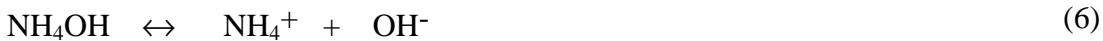
Makeup water sample



Cation conductivity sample



Specific conductivity sample



Cation Conductivity Temperature Compensation

A cation conductivity sample is different. It has had ammonia and/or amines removed and any salts converted to acids. The ionization of acids and water cannot be neatly separated for compensation since they have hydrogen ion in common. As a simplified example, see equations 3 and 4. The additional hydrogen ions from the acid suppress dissociation of 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 goal was to be able to compensate trace acids 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 since the hydrogen ion has the dominant concentration and the dominant ionic conductance. The anion is of secondary importance. Thus sulfuric and other acids would have very similar conductivity/temperature characteristics.

The first cation conductivity temperature compensation algorithm was developed about 16 years ago using the best curve matching that could be developed at that time.⁴ In the intervening years, a number of other attempts have been made at providing this compensation. An excellent compensation match to hydrochloric acid in pure water across the full ranges of temperature and concentration was finally achieved. A comparison of the compensation algorithms of several instruments, with hydrochloric acid data as the reference, was made. Appropriate simulated resistances and temperature signals were used as input to several manufacturers' instruments and the resulting compensated conductivity readout was recorded and compared with the theoretical values. In Figure 4 it can be seen that a vast improvement has been obtained, indicated by the results with the Thornton algorithm in instrument E.⁵ It is apparent that temperature compensation is by far the greatest source of error in cation conductivity measurement with most instruments installed in power plants today.

While temperature compensation with accurate algorithms can eliminate substantial errors in the measurement, it should be stressed that reasonable sample temperature control 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. Cation resin performance in high purity waters has been shown to be more sensitive to sample flow velocity and temperature than is widely appreciated. A minimum flow velocity of 30 cm/min in the column is recommended.⁶

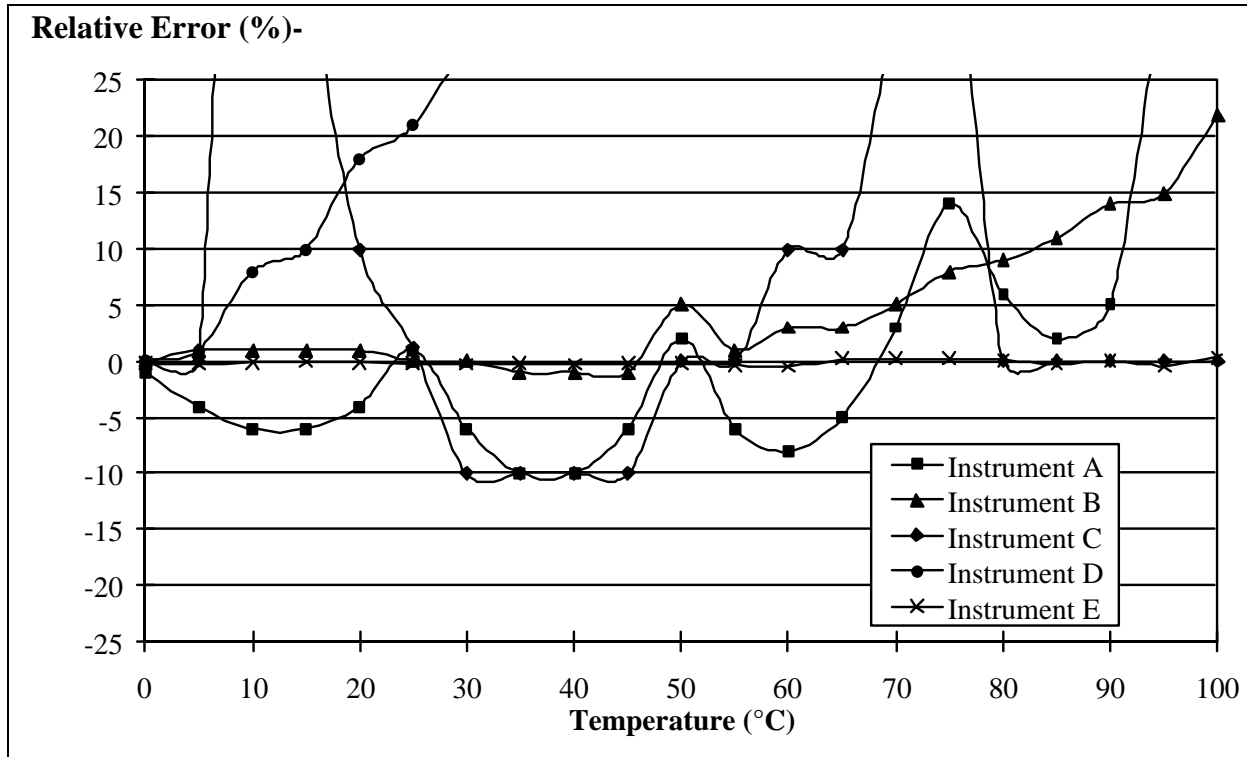


Figure 4 - Comparison of Cation Conductivity Temperature Compensation Performance at 0.1 µS/cm

Specific Conductivity Temperature Compensation

More recently, the above approach was also taken to improve specific conductivity temperature compensation for ammonia. A truly accurate algorithm for ammonia must include the changing dissociation of both ammonia and water and the interaction between them as in the model described by equations 5 and 6. The common hydroxide ion causes the interaction. The relationships can be handled using the appropriate ionic equilibrium equations. The best available data were used for the ion product of water, the dissociation constant for ammonia, the equivalent ionic conductances of hydrogen, hydroxide and ammonium ions, plus the density of water, all varying with temperature. These were used in standard ionic equations to obtain the reference values of conductivity vs. temperature at various low concentrations of ammonia.

These reference values were used in the development of a proprietary and precise compensation algorithm. It relates the uncompensated conductivity and temperature of low concentrations of ammonia to their conductivity at 25°C. This algorithm is able to track the

properties of ammonia and water very closely even to extreme operating conditions as shown in Figure 5. Other instruments evaluated for specific conductivity had similar errors to those shown in Figure 4 for cation conductivity.⁷

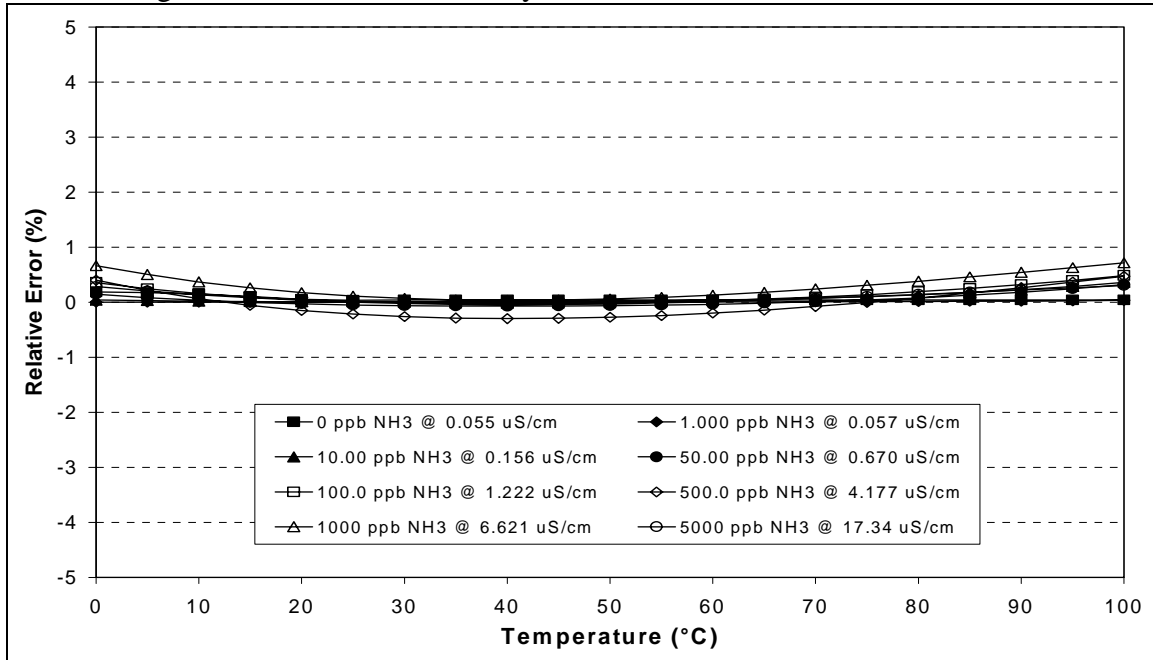


Figure 5 - Instrument E Specific Conductivity (Ammonia) Temperature Compensation Performance

It is clear that very significant errors occur in widely accepted equipment for specific and cation conductivity measurements in power plants. In fact, temperature compensation is the largest source of error, by at least an order of magnitude, in these measurements. It is hoped that future instrument evaluations will look deeper into temperature compensation performance for specific types of samples.

Practical Impact of Inadequate Temperature Compensation

A large Asian power plant and its suppliers experienced some far-reaching problems with poor temperature compensation of cation conductivity. Condensate polishers were supplied with a new 500 MWe unit provided as a part of continued expansion of the site. Cation conductivity instrumentation to monitor the individual polisher vessel outlets was included to assist in the operation and management of the polisher system which was designed to operate in the ammonia cycle during periods of steady-state operation of the unit. During commissioning of the system, the “dilute acid” algorithm was selected on the instruments and the initial cation conductivity values for polishers operating in the hydrogen cycle with freshly regenerated resin charges could not achieve indicated values below the 0.150 $\mu\text{S}/\text{cm}$ range and the observed values were not stable.

Investigation soon revealed that the temperature of the sample stream flowing through the cation column and cell was in the 40-50°C range and tended to fluctuate with outside

temperature and unit operating conditions. Furthermore, the conductivity instrument was one of the poor performers illustrated in Figure 4. To verify that temperature compensation was at fault, an ice bath was set up to obtain temporary sample cooling closer to 25°C. This, in combination with a change of the temperature compensation algorithm from “dilute acid” to “neutral salts,” brought the cation conductivity reading down to the 0.06-0.07 $\mu\text{S}/\text{cm}$ range as expected. This information led to a decision to move the conductivity instrumentation to a sampling room where “constant temperature” baths are available to reduce the temperature of the sample streams to the 20-25°C range. Additional studies to determine the best ultimate solution are still in progress.

While this example gave readings indicating worse quality water than actually existed, Figure 4 shows that some errors can also occur in the more dangerous direction, indicating better water quality than actually exists—with the potential for causing unexpected corrosion damage. There are a myriad of severe consequences that erroneous conductivity measurements could entail, including: failure to meet boiler and turbine warranty requirements, poor performance against EPRI or ASME guidelines, wasted time troubleshooting problems that don’t exist, operators conditioned to ignore measurements, etc.

Finally, some operations such as oxygenated treatment or operation of once-through boilers and other devices which are sensitive to ppb or sub-ppb concentrations of chlorides and other strong acid forming anions, require very accurate measurement of cation conductivity. It appears doubtful that sample stream temperature adjustment alone, while it certainly represents a valuable first step toward providing stability, will result in an environment in which the readings are sufficiently stable and accurate to be of use in estimating the concentration of chlorides and other anions in the 0-10 ppb range. Figure 6 illustrates the potential sensitivity of cation conductivity in this range when it is measured accurately.

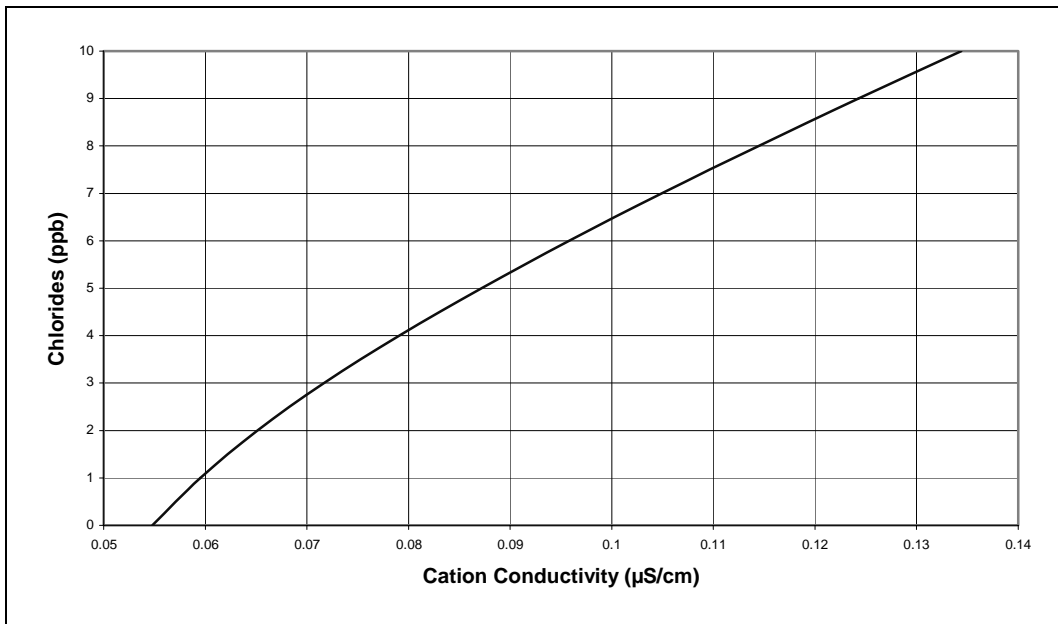


Figure 6 - Cation Conductivity Expressed as Chlorides⁸

CONCLUSION

The accuracy of conductivity measurements, the reliability of analytical results and operators' confidence in them all depend on higher performance of this kind of instrumentation. A conductivity troubleshooting guide is provided in the appendix for quick reference on typical problems.

The upgrade of conductivity equipment and its maintenance is well-justified. Ultimately, safe operation and the life of power plant components depend on using these improvements.

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Appendix - Troubleshooting High Purity Conductivity Measurements

Symptom	Possible Cause—Corrective Action
Grab sample conductivity reads higher than on-line sample	<ul style="list-style-type: none"> • Grab sample is exposed to air too long, allowing significant absorption of CO₂.—Seal grab sample better or measure from flowing sample. • Grab sample sensor and/or container are contaminated.—Rinse longer. • Portable instrument has inadequate temperature compensation.—Use on-line instrument type as portable.
Grab sample conductivity reads lower than on-line sample	<ul style="list-style-type: none"> • Portable instrument has inadequate temperature compensation—Use on-line instrument type as portable.
Conductivity reads high or off-scale	<ul style="list-style-type: none"> • DI Resin beads or fines are trapped between sensor electrodes—Clean sensor. • Instrument has inadequate temperature compensation.—Check setting, replace instrument.
Conductivity reads low or cycles down and up	<ul style="list-style-type: none"> • In makeup water, gas bubbles form in the sensor due to pressure drop, temperature rise and/or CO₂ release. When bubbles are large enough, they dislodge and new ones begin to form. Repetition of this causes cycling.—Increase flowrate and/or relocate sensor into more turbulent flow to carry away bubbles. • In makeup water system, sensor is located in or after a “deadleg” which is very slowly rinsed after regeneration.—Revise piping. • Cable between instrument and sensor is too long—limit length to system specifications. • Instrument has inadequate temperature compensation.—Check setting, replace instrument.
Conductivity is flow sensitive	<ul style="list-style-type: none"> • <i>Transient</i> flow sensitivity with pure samples is normal due to changing turbulence and contaminants released from fittings, etc which cause the sample composition to change. The measurement itself is not flow sensitive. • Long sample lines with deposits can absorb/release ions depending on flow, like a chromatograph—Clean the sample line and establish constant flow in the main line. • Cation conductivity requires sufficient flow through the resin to achieve good exchange—set flow for > 30 cm/min in column.