Accurate conductivity measurements are critical to the reliable operation of steam electric power plants. In fact, conductivity is the single most important measurement for monitoring water quality in boiler water, boiler feedwater and steam condensate. Water in these systems frequently contains no more than 10 to 20 parts per billion (ppb) dissolved solids, sometimes much less. It is in these high-purity, low-conductivity waters that measurement accuracy is so vital and yet so challenging to verify. Experience and experimentation have shown that some calibration procedures and techniques for verifying measurement accuracy still common in the industry today can lead to expensive results.

For instance, some plant operators continue to use so-called “standard” low-conductivity solutions down to 10 µS/cm in their verification procedures. Research, however, raises serious question as to whether these solutions can be relied on for truly accurate calibrations. Others put faith in grab-sampling techniques even though contamination by residue in the sample container and the rapid absorption of carbon dioxide from the atmosphere are well understood.

Since the health of expensive equipment such as turbines, boilers and condensers depends on accurate conductivity analysis, these traditional methods can have a direct and detrimental effect on a plant’s availability to generate and sell electricity. Therefore, it is material to ask: “What are the practical tolerances of low-conductivity standards,” and “What are the best practices for verifying the accuracy of critical conductivity measurements in high-purity water?”

BingNing Li, control mechanic at Hawaiian Electric Co., gives one example of the sort of maintenance shop paralysis that can result from leaving these questions unanswered. “Our online boiler water conductivity and cation conductivity readings were suggesting a problem, but we were unable to prove their accuracy to justify corrective action.” His colleague, Urwin
Transfiguracion said, “Taking grab samples to a benchtop instrument for high-purity conductivity calibration or measurement verification is unreliable due to CO₂ contamination.” He added, “Decisions to make changes that affect steam cycle chemistry need to be well informed and timely to avoid costly damage to expensive equipment like our boilers and turbines, not to mention the potential for an unplanned shutdown.”

These kinds of problems prompted Emerson Process Management to undertake a study in cooperation with a Southern California Edison laboratory to determine the accuracy of low-conductivity standard solutions.

**Standard Solutions Study Methodology**

Standard solutions tested in this study were purchased from common laboratory supply catalogs and from specialty chemical companies, as any power plant professional would do. Conductivity solutions from three sources were tested in Emerson Process Management analytical laboratories and then verified in the water chemistry labs of Southern California Edison. The stated conductivity value and tolerance for each solution was taken from the certificate of analysis affixed to its container.

Sealed containers of solution standards were placed in a constant temperature bath to adjust their temperatures to 25.0 C plus or minus 0.05 C. The containers were periodically shaken to ensure proper mixing and ample time was allowed for temperature stabilization. Conductivity measurements were taken immediately after breaking the container’s seal.

The solutions were measured with certified reference lab cells and conductivity bridges. The reference cells were calibrated using the widely accepted American Society of Testing and Materials (ASTM) D1125 methodology using National Institute of Standards and Technology- (NIST-) traceable lab devices and glassware for the standard cell calibration. The reference bridges were calibrated with NIST-traceable resistors of plus or minus 0.1 percent tolerance. The two laboratories conducted tests completely independent of one another, each using its own reference cells, conductivity bridges, lab equipment, supplies and quality systems. The total uncertainty in the laboratory measurements was less than 1 percent.

**Standard Solutions Study Results**

In nominal 10 µS/cm solutions, most pertinent to high-purity water analysis, the study data indicated substantial differences between the stated conductivities and the actual conductivities measured. The errors ranged from 34 to -0.9 percent with the majority in excess of 11 percent. Only four samples from one vendor were verified to be within 2 percent. Unfortunately, those results were not consistent even within the same batch, with errors up to 5 percent. Clearly, the magnitude of these errors is unacceptable.

In nominal 100 µS/cm solutions the errors were much smaller ranging from 0.1 to -3.3 percent with the majority less than 1 percent. Only three samples from one vendor were verified to be outside 2 percent. With these limited errors, the study indicates that a carefully selected 100 µS/cm conductivity solution can be used for an accurate calibration (within 2 percent). Although a reasonable standard, the 100 µS/cm solution has limited power industry application because it is well beyond the range of interest (high-purity and ultra-pure water). Full study results are available by contacting the author.

This study’s findings support published recommendations of the American Society of Testing and Materials (ASTM) that state “… due to the high uncertainties of atmospheric and container surface contamination, direct cell calibration with standard solutions below 100 µS/cm is not recommended.” Note that solutions of 100 µS/cm are acceptable where applicable. While opening a standard solution and exposing it to carbon dioxide is the most commonly recognized form of contamination, the excessive errors found in the study in 10 µS/cm solutions can likely also be explained by container contamination,
Clearing the Confusion

Whether the power plant chooses to set up the ASTM methodology on its own or buys a commercially available conductivity validation instrument, this approach may well end the confusion and concern that high-purity water conductivity analysis has generated in recent years. According to James Wong of Hawaiian Electric, the use of a portable conductivity validation kit “… gave us the confidence we needed to determine that our boiler water chemistry was trending out of control.” Since the importance of accurate conductivity analysis in the power plant cannot be overstated, and because the seemingly obvious approach to calibration is demonstrated not to be accurate in high purity water, finding an appropriate verification methodology that’s both simple and cost-effective gives power plant engineers one less thing to worry about.

The health of expensive equipment such as turbines, boilers and condensers depends on accurate conductivity analysis

method is detailed in ASTM Method D1125, which describes a calibration procedure based on a comparison with a calibrated conductivity cell. Figure 1 illustrates a laboratory setup using this approach. The cell (or loop) under test is compared against a certified reference analyzer and cell. Both cells are placed in the same sample and agitated. The water’s exact conductivity and temperature are not critical because both cells are exposed to the same conditions at the same time. The exact cell constant of the test cell can be derived from the difference in conductivity readings between the loops. For loop calibration, the test loop’s conductivity reading can be standardized to that of the reference loop.

Similarly, comparing the test instrument against a certified reference instrument can be performed without taking the test instrument out of the process. This method requires the availability of a sample tap near the test cell and specialized conductivity reference instruments. Portable conductivity validation instruments are commercially available for on-line verification testing. Using this method, a certified reference flow-through cell is connected to the sample tap. The process water is passed directly from the sample tap through tubing to the flow-through cell and then to drain, as seen in Figure 2. The process water is, therefore, isolated from interferences. The conductivity reading from the reference instrument and the unit under test can then be analyzed to determine the test sensors’ cell constant or to calibrate the loop.

An Alternative Method

By accepting that standard solutions are not an accurate calibration method below 100 µS/cm, making them inappropriate for most power industry applications, what then is an effective alternative? One method is detailed in ASTM Method D1125, which describes a calibration procedure based on a comparison with a calibrated conductivity cell. Figure 1 illustrates a laboratory setup using this approach. The cell (or loop) under test is compared against a certified reference analyzer and cell. Both cells are placed in the same sample and agitated. The water’s exact conductivity and temperature are not critical because both cells are exposed to the same conditions at the same time. The exact cell constant of the test cell can be derived from the difference in conductivity readings between the loops. For loop calibration, the test loop’s conductivity reading can be standardized to that of the reference loop.

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Steam Generation: An Overview

Corrosion related failures cost the power industry billions of dollars every year. Good water chemistry reduces corrosion, but it is not possible without the continuous monitoring of pH, conductivity, cation conductivity, degassed cation conductivity, and dissolved oxygen.

MEASUREMENTS
- Chlorine
- Conductivity
- Dissolved Oxygen (ppm, ppb)
- Hydrazine
- ORP
- pH
- Phosphate
- Silica
- Sodium
- Turbidity

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