

# NEW LEVEL OF WATER CHEMISTRY SAFETY COMPLIANCE WITH ON-LINE CHLORIDE AND SULFATE MEASUREMENT

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## INNOVATIVE TOOLS & TECHNIQUES & NEW O&M PRACTICES

This paper/presentation will review the evolution of power plant analytics and how they are improving key measurement parameters to better manage and control corrosion in today's power plants. This evolution has continued now to the point where plants can now directly measure the most corrosive contaminants of chloride and sulfate with semi-continuous on-line monitoring instrumentation. This new technology will then be reviewed in more detail.

As a result, monitoring of chloride and sulfate at very low ppb limits has been specified as part of steam cycle chemistry guidelines from VGB, EPRI, IAPWS and other leading standards organizations.

New technology into this online analyzer is based on microfluidic capillary electrophoresis. This paper will highlight the advantages of this technology vs. traditional indirect methods as well as expensive and labor intensive laboratory testing. In addition, it will share how modern supercritical and nuclear plants can use these new analyzers to meet regulatory compliance and safe water chemistry operating conditions.

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### Introduction

If you haven't been watching closely you may have missed a significant evolution in the quality, accuracy and technology around power plant water chemistry analytics. While some vendors have been satisfied to continue to sell the same basic analog and often inaccurate equipment for the last 20 years. A leading supplier in this space has introduced many new technology advancements to help power plants better manage and control water chemistry with more measurement confidence. While at the same time have moved expensive or complicated laboratory tests to online and real-time monitoring of water and steam quality.

Some tangible examples of this evolution, include the transition from analog to digital sensors, the development of the new generation of sensors designed for faster response and accuracy in ultrapure low conductivity water, the development of multi-channel multi-parameter transmitter's with powerful built in calculated/computed values that provide additional value, the capabilities to thoroughly validate chemistry alarms before false alarms are sent to the control room, sensors and analyzers that can do self diagnostics, reducing and optimizing maintenance cycles while providing a path away from non-specific representative measures like the specific and cation conductivity. This evolution now provides the ability to move away from grab a sample laboratory-based testing for contaminants like TOC (total organic carbon), chloride and sulfate with sensors and analyzers that make it possible to be measured directly and specifically online. This paper will now review in detail the new technology that allow for online, low ppb level measurements of chloride and sulfate.

### Chloride/Sulfate Measurements Become Increasingly Important

Chlorides and sulfates have been identified for decades as some of the most corrosive contaminants in power plant water. Various forms of damage to plant assets can be traced back to the effect of these contaminants. Pitting, stress corrosion cracking and other corrosion mechanisms attack boiler and steam generator tubes, turbines and other key components in the steam-water cycle. Deposited corrosion products cause further losses through under-deposit corrosion, lowered efficiency and more frequent shutdowns for cleaning.

With the growth of supercritical and ultra-supercritical plants, there has been a renewed focus on keeping these dangerous contaminants as low as possible and responding quickly when alarms are

triggered indicating that levels are too high. This is a similar state to what has been practiced in Nuclear plants around the world. In Nuclear plants however, they traditionally have been forced to do grab sampling as often as every 4hrs and employ multiple, expensive Ion chromatography units.

Another contributing factor to this issue is the requirement for more frequent cycling at power plants, leading to frequent load changes, startups and shutdowns. The unpredictability of solar and wind generation as well as market pricing fluctuations in regions with competitive power generation require thermal power plants to meet demand as needed and with rapid response. Shutdowns frequently involve air intrusion with accompanying oxygen and carbon dioxide that aggravate corrosive conditions. Thermal expansion and contraction of components cause loss of passivated layers. Startups are often rushed to respond quickly to demand and maximize return during high market price periods, but fast startups push the limits on steam quality. More frequent cycling results in longer duration of operation under these more corrosive conditions. Power plants are constantly pressured to balance power plant asset protection from such conditions with the need to generate electricity quickly to maximize revenue.

All of these needs and effects are good justification for the recommended low single-digit ppb limits for chloride and sulfate in boiler feedwater and steam in the various cycle chemistry guidelines and turbine warranty requirements.

For more comprehensive monitoring of these conditions in cycle chemistry and to manage profitable generation without compromising plant assets, more meaningful analytical measurements are a key tool. A direct on-line measurement of chlorides and sulfates goes a long way toward clarifying how fast a startup can proceed and can quickly detect contaminating conditions with high sensitivity during normal operation.

### **Existing Measurement Technologies Fall Short**

With the lack of practical on-line chloride and sulfate measurements, cycle chemistry guidelines have relied on inferred measurement such as cation conductivity.

CATION CONDUCTIVITY measurement is a continuous, fast-responding, low-maintenance parameter that eliminates interference from ammonia and/or amines by cation exchange, but detects all anions in the sample including carbon dioxide, primarily in the form of bicarbonate ion. Its sensitivity is enhanced by converting the anions to their more conductive acid form but there is no way to know the conductivity contribution from each anion, whether it's from corrosive chloride and sulfate, less corrosive acetate and formate (from breakdown of amines) or virtually harmless bicarbonate.

As a result this ambiguity, cation conductivity guidelines have been written loosely allowing them to be achieved realistically with the measurement technology that has been available thus far. However, these guidelines do not correlate with the purity levels actually needed to minimize corrosion and that are desired by turbine manufacturers: typically less than 2 to 5 ppb of chloride and sulfate.

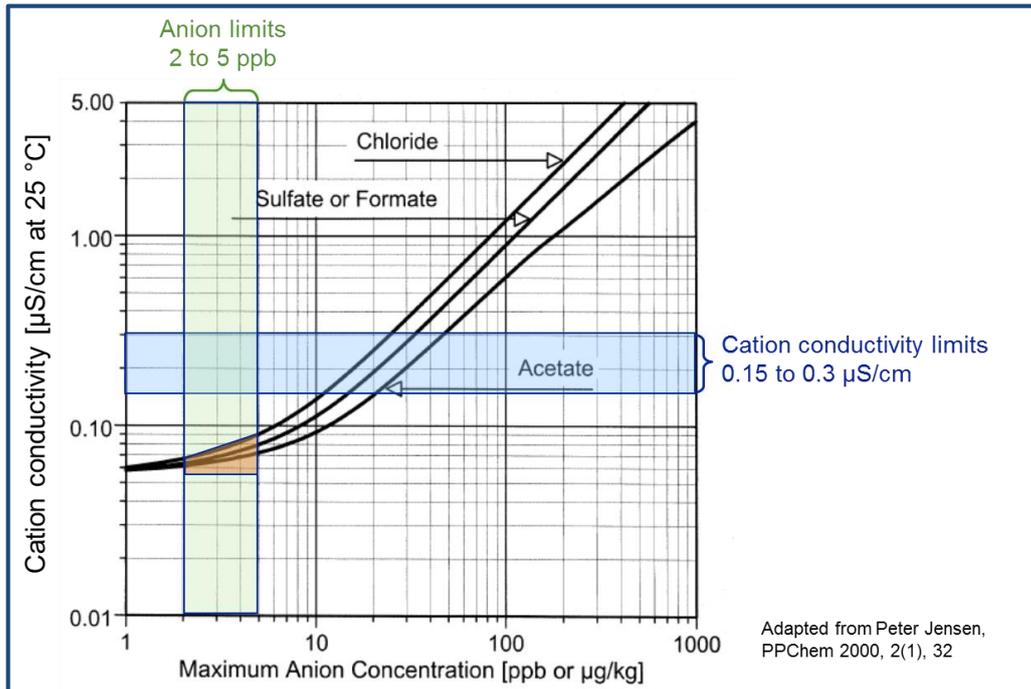


Figure 1 : Anion limits Vs. Cation Conductivity limits

Figure 1 shows the conductivity of chloride, sulfate, formate and acetate ions in their acid form, with typical conductivity and anion concentration limit ranges shown as shaded bands. If all of the conductivity were due to these anions, it can be seen that cation conductivity limits of 0.15 to 0.3  $\mu\text{S}/\text{cm}$  would allow much higher concentrations than are desirable as shown in Table 1.

Table 1 : Cation conductivity measurements and corresponding contaminant concentration

Anion	Cation Conductivity ( $\mu\text{S}/\text{cm}$ at 25 °C)			
	0.15	0.2	0.3	0.5
Chloride, ppb	12	17	25	43
Sulfate, ppb	14	22	33	57

In fact, operation should be confined closer to the orange shaded area in Figure 1 if all the conductivity were due to chloride and sulfate. Of course any conductivity measurement  $< 0.055 \mu\text{S}/\text{cm}$  is not possible. There is clearly a disconnect caused by the inability to specifically measure corrosive anions and the fallback of using conductivity measurements to infer concentration. In today's world of cycling plants generating corrosive conditions for longer periods of time and of increased use of amines, the use of degassed cation conductivity may be ideal for a quick indication of decrease in corrosive conditions during initial stages of startup but it would be incorrect to assume low conductivity measurements correlate to low chloride and sulfate measurements. Direct measurement of chloride and sulfate levels is required to confirm they are within acceptable limits before starting power generation.

Certain current methods of measurement such as ion-selective chloride analyzers and ion chromatography provide identification of specific anions at ppb levels. However, these may either not

have the limit of detection required for such low ppb-level measurements, or are too cost-prohibitive to purchase, operate and maintain both in terms of cost of ownership and trained personnel.

There is still a significant unmet need for specific and sensitive on-line chloride and sulfate measurement instrumentation that has lower capital and operating costs including reduced personnel time and skill requirements. Capillary electrophoresis technology has been developed into standardized instrumentation that is beginning to fill this niche.

### Principle Of Capillary Electrophoresis

Capillary electrophoresis uses an electric field to separate particles or ions in an electrolyte based on their mobilities as in Figure 2. It is primarily the ions that are attracted through the capillary, not the bulk sample so that suspended particles are less of a concern. The ions eventually pass a conductivity detector near the end of the capillary where the response could be used to generate an electropherogram similar to an ion chromatogram.

Early research and development on this technology for power cycle chemistry measurements was initiated at the Colorado State University, USA.(Ogan, Palmer, Dekleva, 2012) (Palmer, Dekleva, Heim, Ogan, 2013).

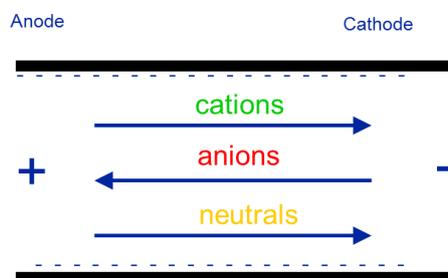


Figure 2 : Capillary Electrophoresis Concept

### Capillary Electrophoresis Implementation

To develop practical on-line instrumentation using capillary electrophoresis technology, the high voltage electrodes and capillary must be capable of continuous operation with sample and electrolyte replenished with each measurement cycle. These requirements are achieved with a design using a replaceable microfluidic capillary cartridge that provides fresh electrodes, clean capillary and solution reservoirs. The cartridge and its operation are shown in Figure 3.

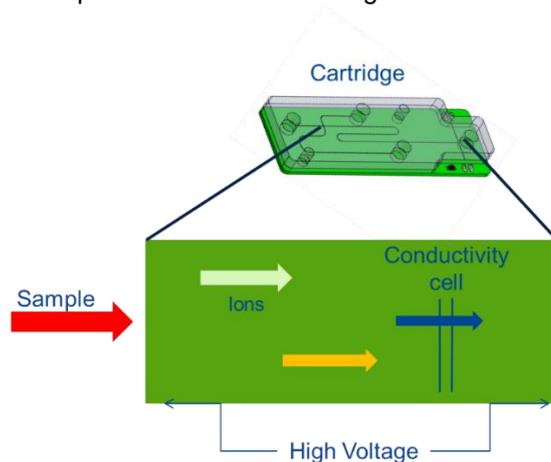


Figure 3 : Microfluidic Capillary Electrophoresis Cartridge

### Measurement Process

As discussed earlier, the various types of ions travel through the capillary on the cartridge under the influence of an electric field and eventually arrive at a conductivity detector. Based on their mobilities, the ions always arrive at the detector in the same order to provide identification and the conductivity

response indicates the concentration. The voltage continues to purge all extraneous ions from the capillary, preparing it for the next measurement cycle. Conductivity peaks for each ion, including an internal standard solution, are measured and processed to obtain the chloride and sulfate concentrations as shown in Figure 4. The display, alarms and outputs are updated and held at the new measured values with each cycle. The entire measurement cycle is accomplished in 15-45 minutes.

Comprehensive details on all steps of the analyzer operation and measurement process were presented by David Gray and Akash Trivedi at the International Water Conference, San Antonio, Texas, USA (November 2016).

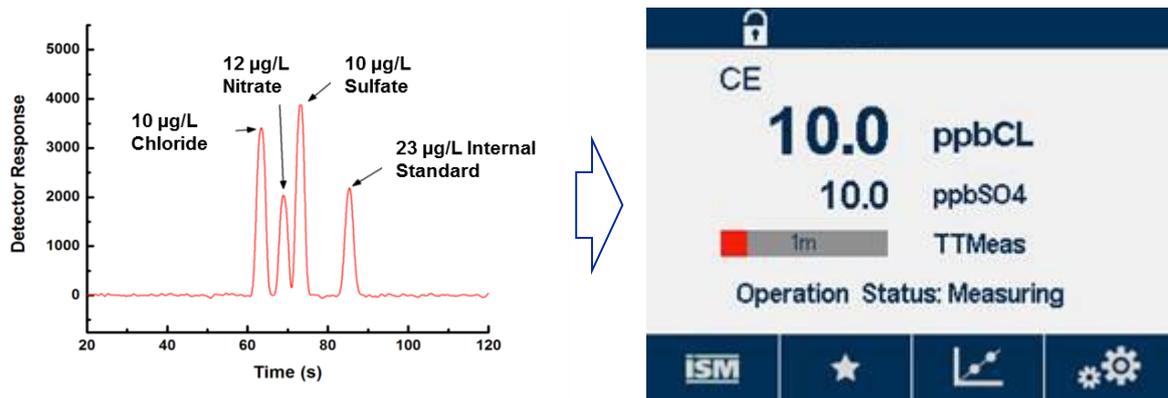


Figure 4 : The internal electropherogram is processed to obtain direct concentration readout

### Analyzer Details

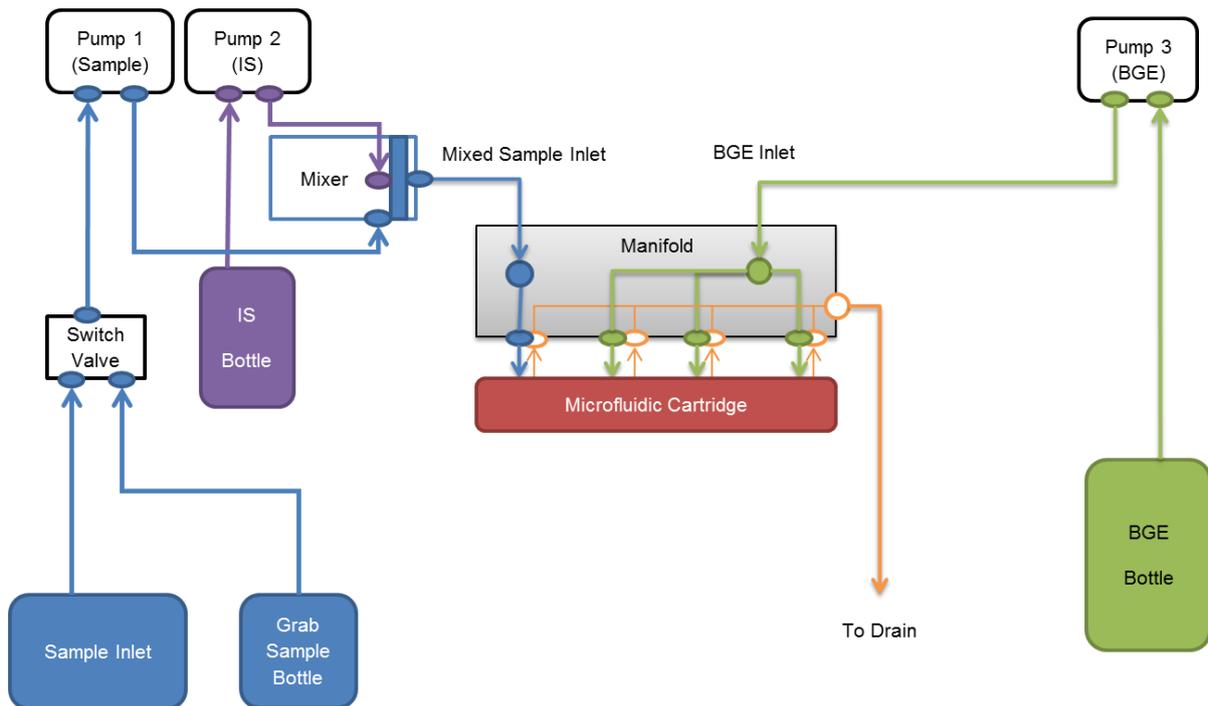


Figure 5 : Components of the Chloride/Sulfate Analyzer

The various parts of the analyzer are shown in Figure 5. A coarse suspended particles filter removes any large particles in the sample. The microfluidic capillary cartridge is the heart of this new analyzer platform and can measure chloride and sulfate in the range of 0-500 ppb. The cartridge is replaced approximately once every 2 months, depending on the frequency of measurement. Reagents include the background buffer electrolyte and the internal standard solution that are used with every measurement, and are refilled typically every 2 months. The grab sample provision also enables measurement of a chloride/sulfate standard solution for periodic verification or calibration. The

chloride/sulfate analyzer can be used with an external multi-stream sequencer to measure multiple sample water streams using a single analyzer. The transmitter/display module uses a color touch screen with direct readout and trending of ppb chloride and sulfate and provides straightforward menus for setup and operation. The transmitter includes multiple relays and 0/4-20 mA output signals for alarming and retransmission of concentration data.

### **Power Plant Evaluation**

An early model of this analyzer was evaluated at four different power plants with varying water chemistries and fuel sources. Working with different partners, the analyzer's performance was demonstrated to provide consistent results and the measurements compared to cation conductivity or ion chromatography where available. With different additives used at these power plants, the analyzer's operation in the presence of those additives was also evaluated and quantified.

CASE STUDY #1 : Performance evaluation at nuclear power plants was conducted by Electric Power Research Institute – EPRI in 2016 in collaboration with their member, Exelon. As part of EPRI's efforts to automate sample measurements in nuclear plants and convert such measurements from laboratory-based to on-line, the microfluidic capillary electrophoresis technology was evaluated in 2015 as a potential candidate for further testing. By moving to on-line measurements, EPRI and its members aimed to reduce radiation exposure for plant personnel and enable continuous monitoring of plant conditions that was not available with laboratory-based testing using grab samples.

The chloride/sulfate analyzer was chosen for further testing to prove its performance in power plants, leading to field evaluations in 2016. The analyzer was installed and operated at two nuclear power plants owned and operated by Exelon – Byron, Illinois (USA) and Quad Cities, Illinois (USA). Byron is a Pressurized Water Reactor nuclear power plant and Quad Cities is a Boiling Water Reactor nuclear power plant.

Comprehensive testing was conducted at both sites by EPRI's lead contractor, Finetech, and the test data, statistical comparison to ion chromatography data from tests conducted on the same samples and results have been published by EPRI on March 31, 2017 in their report "Demonstration of Microchip Capillary Electrophoresis for Chloride and Sulfate Analysis" (Report No. 3002010295). A summary of the report was presented by Joel McElrath of EPRI at the International Conference On Cycle Chemistry Instrumentation, Monitoring and Control organized by EPRI May 2-3, 2017 in San Antonio, Texas (USA).

The key findings presented from the evaluation were :

- Early data shows comparable results to grab samples analyzed by ion chromatographs.
- The analyzer offers quick analysis with results available in as little as 15 minutes.
- Its small footprint and small sample volumes allow effective use in sample panel rooms and limited use of sample water.

Based on the field evaluation experience and results, EPRI also identified a number of improvements to the analyzer to enable it to perform more effectively across power plants and their associated water chemistries :

- During the evaluation, it was noted that sample flow to the analyzer stopped from the power plant sample panel causing the analyzer to run dry without providing an alarm to the user. A sample flow control and alarm would provide the user with adequate notice to take corrective action.
- The data processing for sulfate measurements required upgrading to provide more stable measurements with higher levels of accuracy.
- Performance of the analyzer should be demonstrated in the presence of a variety of additives, to ensure they do not impact measurements or cause interference in the measurement process

Focusing on this feedback from EPRI, enhancements have been made to the analyzer to address this input as well as ensure performance stability and reliability :

- A flow check valve has been incorporated in the analyzer to prevent sample water to flow out of the analyzer and preventing it from running dry. Moreover, a flow sensor has been provided to generate an alarm in case sample flow stops, thereby alerting the user to take

corrective action. This ensures the analyzer will not run dry and damage the microfluidic capillary electrophoresis cartridge.

- The data processing for sulfate measurements has been improved to provide more stable and accurate measurements. The chloride measurement stability has not been altered, and continues to provide reliable measurements at low ppb levels.
- The analyzer is being evaluated in a variety of water chemistries using samples from a number of power plants as well as by using samples prepared in the laboratory that are similar in composition to typical power plant samples. This will continue as an on-going exercise as new additives available to the industry are tested and the analyzer performance demonstrated in their presence.

EPRI has scheduled a field evaluation of the analyzer with these enhancements at Ameren's coal-fired power plant in Labadie, MO, and the tests will commence on July 12, 2017.

**CASE STUDY #2 :** An evaluation at a coal-fired power plant was conducted next in consultation with Brad Buecker, Process Specialist at Kiewit Power Engineers. The Nearman Creek Power Plant at Kansas City, Kansas (USA) was identified as a test site for the chloride/sulfate analyzer. Nearman Creek Power Plant is owned by the Board of Public Utilities, Kansas City, Kansas, and uses coal as its fuel source. It is a 261 MW power plant with an operating pressure of 1860 psi and has been in operation since 1981.

As it prepared for a planned shutdown for maintenance and replacement of the turbine, the power plant identified a need to measure chloride and sulfate levels to ensure that their plant assets were not being exposed to unacceptable levels of these corrosive contaminants. The power plant currently uses cation conductivity measurements to monitor contaminant levels. However, the plant also uses methoxypropylamine in its water chemistry, which undergoes thermal decomposition into acetate and formate ions. These acetate and formate ions add to the cation conductivity measurement, thus elevating it to higher than acceptable levels while masking the true levels of chloride and sulfate in the water as measured by cation conductivity. As a result, the cation conductivity measurements for the main steam sample line were consistently above 2.5 uS/cm, well beyond acceptable limits of 0.15-0.3 uS/cm as specified in various industry guidelines.

The chloride/sulfate analyzer was installed in August 2016 on the main steam sample line in parallel to the cation conductivity measurement, to analyze the contaminant levels. After the initial rinse-down period, the analyzer operated consistently to provide reliable and accurate measurements of chloride and sulfate ions in the sample as shown in Figure 6. The power plant could confirm that their chloride and sulfate levels were within acceptable limits of 2-3 ppb as defined by industry guidelines.

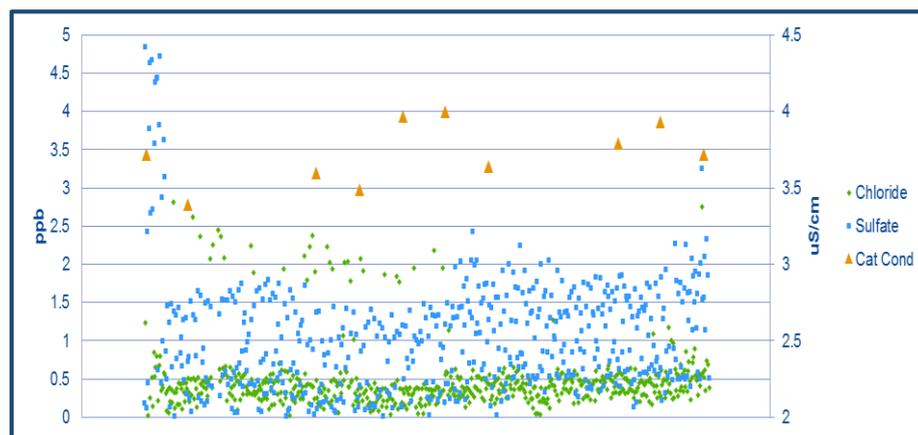


Figure 6 : Chloride, Sulfate & Cation Conductivity measurements for main steam, Nearman Creek Power Plant, Kansas City, Kansas (USA)

This field evaluation of the chloride/sulfate analyzer demonstrated performance in presence of a commonly used amine in power plant water chemistry, while assisting in identifying low ppb-levels of chloride and sulfate contamination. Further evaluation of power plant water conditions will be

conducted once the power plant resumes operation and continues power generation consistently without cycling.

CASE STUDY #3 : A performance evaluation at a biomass power plant was the focus of collaboration with Engie. The PineTree Power Plant at Tamworth, New Hampshire (USA) is a biomass power plant using waste wood chips as its fuel source. It is a 25 MW power plant with an operating pressure of 665 psi and has been in operation since 1987. It was identified as a site for demonstrating the performance of the chloride/sulfate analyzer while also providing the power plant an insight into its water chemistry and contaminant levels. The power plant does not use cation conductivity or advanced measurement methods for chloride/sulfate detection, and the installation of the analyzer provided the first data of the levels of corrosive contaminants in the power plant water. The plant uses NALCO 5711 (a proprietary ammonia and amine blend) in its water chemistry.

After the initial rinse-down, the analyzer performed consistently in the presence of a proprietary blend of additives to provide low ppb-level measurements of chloride and sulfate as shown in Figure 7. The power plant confirmed that chloride and sulfate levels in their water were within acceptable limits, though sulfate levels were close to the maximum acceptable levels.

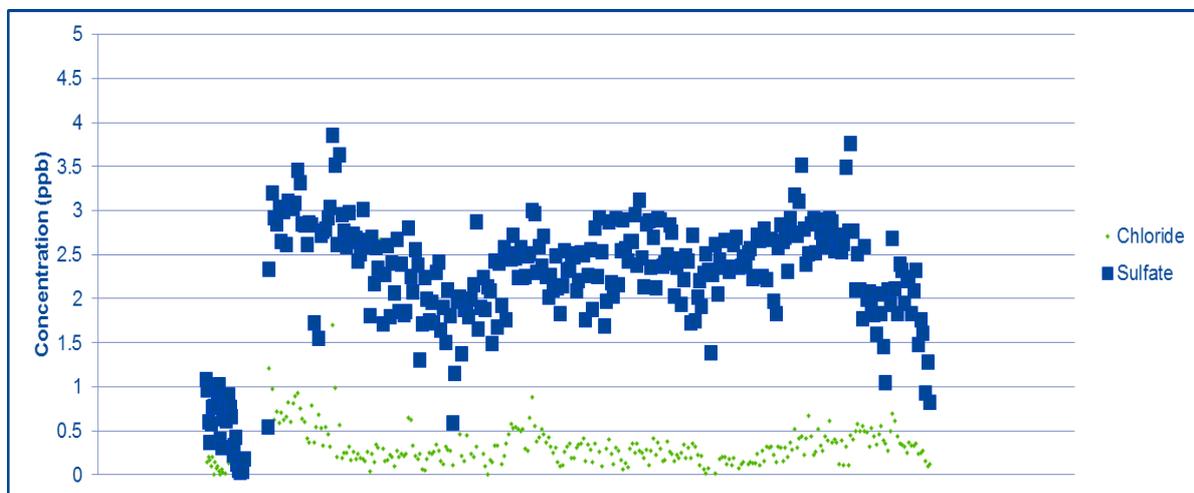


Figure 7 : Chloride & Sulfate Measurements, PineTree Power Plant, Tamworth, New Hampshire (USA)

Further evaluation of long-term performance of the chloride/sulfate analyzer will continue at the power plant, to demonstrate measurement reliability and stability.

### Conclusion

With chloride and sulfate being key corrosive contaminants in power plants, the need to measure their levels has increased with the rise in supercritical, ultra-supercritical, nuclear and power plant cycling as all power plants look to provide greater protection to expensive capital assets. Existing methods to monitor the levels of these contaminants are either a substitute measurement such as cation conductivity, or have a high cost of acquisition and operation. Microfluidic capillary electrophoresis offers a robust on-line measurement method that is easy to use and maintain, with a low total cost of ownership. Performance of the chloride/sulfate analyzer using microfluidic capillary electrophoresis technology was demonstrated in a number of power plants using various water chemistries and with different fuel sources. Further testing is to continue with EPRI and other partners to demonstrate performance in various applications and plant conditions.

## References

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