

A New Method for Corrosion Prevention

On-line Chloride and Sulfate Monitoring

Corrosion monitoring, control and prevention is an on-going battle in today's power plants. Two of the strongest indicators of how well that battle is being waged is to monitor the corrosive salts of chloride and sulfate. If these are at consistent low levels, the power plant water system is at a minimum level of risk. However, at high levels the cost of corrosion and turbine damage in power plants caused by these ions is immense. As a result, monitoring of chloride and sulfate at very low ppb limits is specified as part of cycle chemistry guidelines and turbine warranty requirements.

Demonstrating compliance at these low limits has always been a challenge. IC (ion chromatography) provides the sensitivity needed for chloride and sulfate monitoring at such low limits. However, the costs of acquisition and operation associated with this sophisticated instrumentation places it out of reach of most fossil power plant budgets. Moreover, most of the IC systems acquired were never operated successfully on-line thus resulting in infrequent monitoring.

An alternative approach involves using cation conductivity and degassed cation conductivity to eliminate carbon dioxide interference to make inferred chloride/sulfate measurements. Ion-selective chloride analyzers have also occasionally been used although it is difficult for them to achieve reliable results in the low ranges required.



This paper explores technology for chloride and sulfate measurement that is far more cost-effective and delivers accurate, on-line measurements down to 0.5 ppb: microfluidic capillary electrophoresis.

Corrosive ions

The highly corrosive nature of chlorides and sulfates has been known for decades. 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

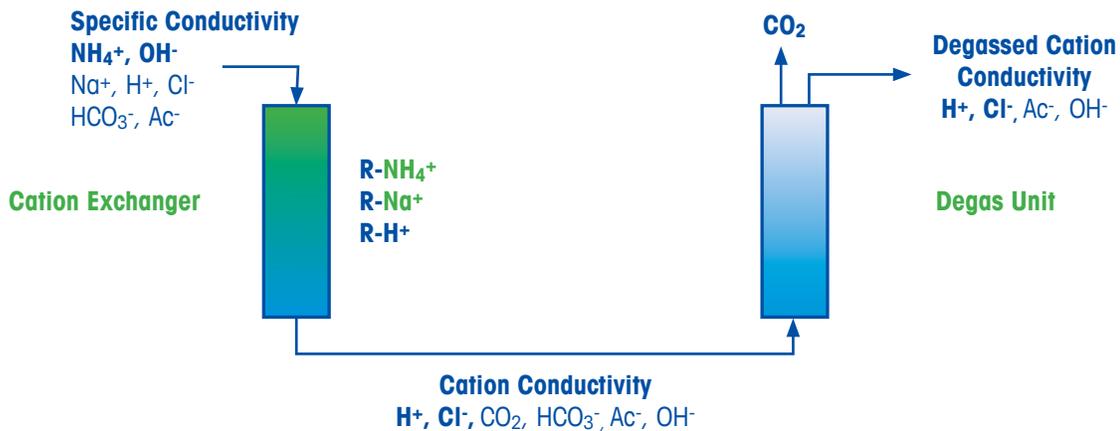


Figure 1 - Cycle chemistry conductivity measurements and representative ionic species contributing to each measurement (R = cation exchange resin, Ac⁻ = acetate)

products cause further losses through under-deposit corrosion, lowered efficiency and more frequent shutdowns for cleaning.

Due to the strong affinity ionic contaminants have for liquid water, seemingly low ppb levels in steam can become very concentrated in the first condensate droplets that form at the final stages of turbines. High chloride and sulfate levels also develop in deposits on metal surfaces where confined water intrusions reach higher temperatures, are boiled away and raise ionic content to increasingly greater concentrations.

A mounting need for specific chloride/sulfate measurement

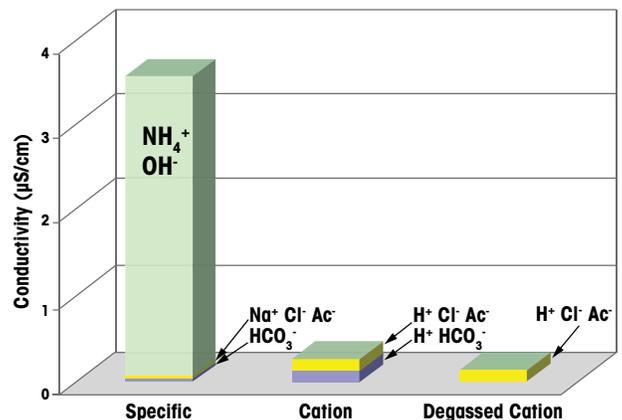
Increasingly, thermal power generation has to compensate for the unpredictability of solar and wind generation. Consequently, a growing number of units operate under cycling conditions, with frequent load changes, startups and shutdowns. Shutdowns frequently involve air intrusion with an increase in accompanying oxygen and carbon dioxide levels that aggravate corrosive conditions. Cycling leads to more frequent thermal expansion and contraction of components, causing loss of passivated layers. Further, startups are often rushed to respond quickly to demand and maximize return during high market price periods, but rapid startup pushes the limits on steam quality that involves tradeoffs between power generation and losses to plant integrity. In short, frequent cycling results in longer operation under more corrosive conditions.

To better understand and manage the compromises between careful chemistry control and short-term power generation, more meaningful analytical measurements are key. Direct on-line measurement of chlorides and sulfates goes a long way towards clarifying how fast a startup can proceed and can quickly detect contaminating conditions during normal operations.

Existing measurement technologies fall short

Due to a lack of practical on-line chloride and sulfate measurements, cycle chemistry guidelines have usually relied on the inferred measurements of cation and degassed cation conductivity (see Figures 1 and 2).

Figure 2 - Representative responses of conductivity measurements (Ac⁻ = acetate)



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 via the cation exchange process but it is not possible to determine the conductivity contribution from each anion, whether from corrosive chloride and sulfate, less corrosive acetate and formate (from breakdown of amines) or virtually harmless bicarbonate.

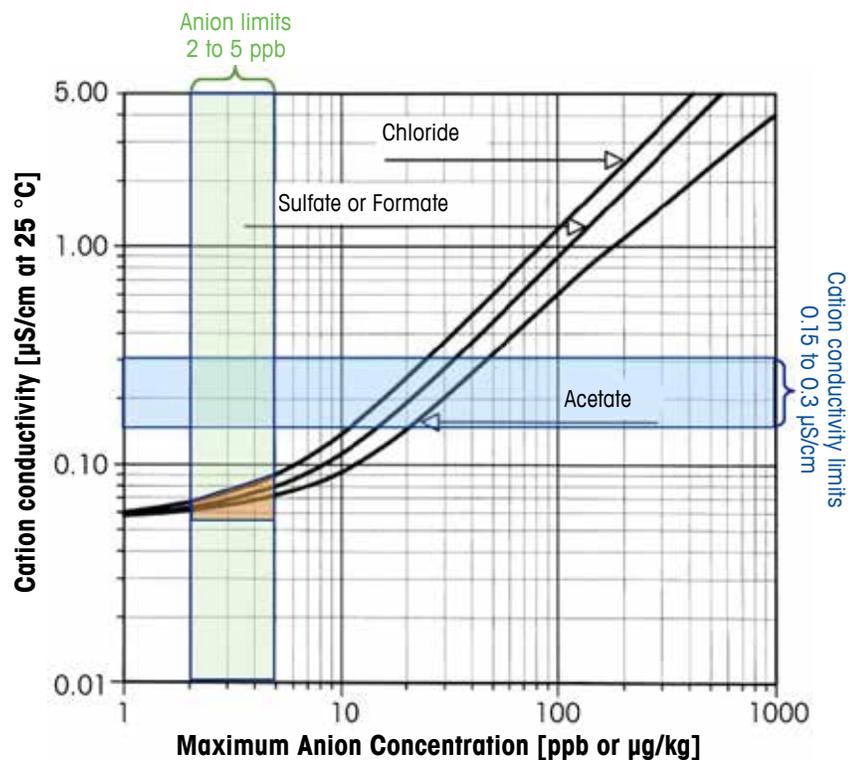
Degassed cation conductivity eliminates the ammonia/amine interference mentioned above and additionally removes carbon dioxide, either by heating or by CO₂-free gas sparging. It provides

low-maintenance, on-line measurement that includes response to chloride and sulfate, but also to acetate and formate as well as any other trace anions in the sample.

As a result of 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, 2 to 5 ppb of chloride and sulfate.

Figure 3 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

Figure 3 - Anion limits vs. cation conductivity limits



Adapted from Peter Jensen, PPChem 2000, 2(1), 32

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. In fact, if all the conductivity were due to chloride and sulfate, operation should be confined closer to the orange shaded area. However, conductivity measurement below 0.055 $\mu\text{S}/\text{cm}$ is not possible. Therefore, there is clearly a disconnect between the inability to specifically measure corrosive anions and the fallback of using conductivity measurements to infer concentration.

Ion-selective chloride analyzers provide a specific on-line response to chloride ion using a solid state ion-selective electrode. But the limit of detection of at least 5 ppb, imposed by the solubility of the sensor element itself, is not adequate to measure high pressure feedwater or steam samples. In addition, an ion-selective electrode does not exist for sulfate, leaving this equally corrosive species undetected. As sulfate can leach from cation exchange resin breakdown in condensate or makeup polishing systems, this creates a very significant measurement gap.

Ion chromatography (IC) instruments can provide excellent sensitivity and selectivity for all the anions of interest if they are equipped with suitable accessories and operated by knowledgeable personnel. However, their use as on-line analyzers is generally impractical. Sample collection as well as operating and maintaining IC equipment is labor-intensive and consequently can be afforded mainly by nuclear plants only. In lean fossil plant chemistry environments, samples are often sent to central laboratories for such analyses in order to avoid the high initial investment of IC as well as operating costs. The inevitable time delays of remote analysis make that information useless for startup decision-making and only gives snapshots of steady operating conditions.

There exists, then, a significant unmet need for specific and sensitive on-line chloride and sulfate measurement instrumentation that has lower capital and operating expenditures. That niche is beginning to be filled by microfluidic capillary electrophoresis (MCE) technology.

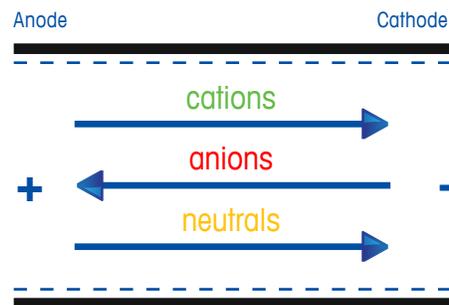


Figure 4 - Capillary electrophoresis concept

Principle of microfluidic capillary electrophoresis

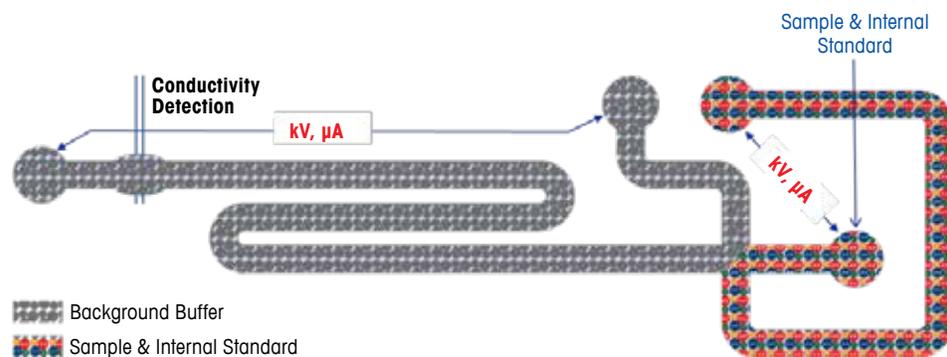
MCE uses an electric field to separate particles or ions in an electrolyte, based on their mobilities (see Figure 4). It has a wide range of applications including DNA fingerprinting, drug analysis and profiling vehicle emissions. The technology has similarities to ion chromatography but also some important differences. IC uses differences in ion exchange selectivity to separate ions as the sample is forced through an ion exchange resin-lined column under pressure. CE, on the other hand, uses differences in electrophoretic mobility to separate the ions as they are pulled through a capillary by high voltage DC.

It is primarily the ions that are attracted through the capillary, not the bulk sample, so the presence of particles is less of a concern than it is in IC. The ions pass a conductivity detector near the end of the capillary where the response can be used to generate an electropherogram similar to an ion chromatogram.

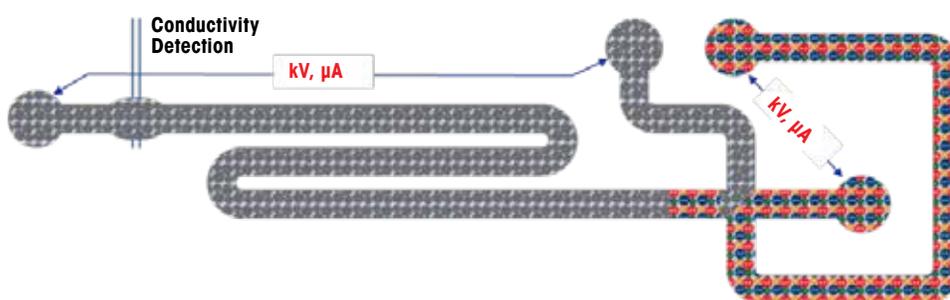
Early research and development on this technology for power cycle chemistry measurements was initiated at the Colorado State University, USA.(1,2)

Microfluidic capillary electrophoresis implementation

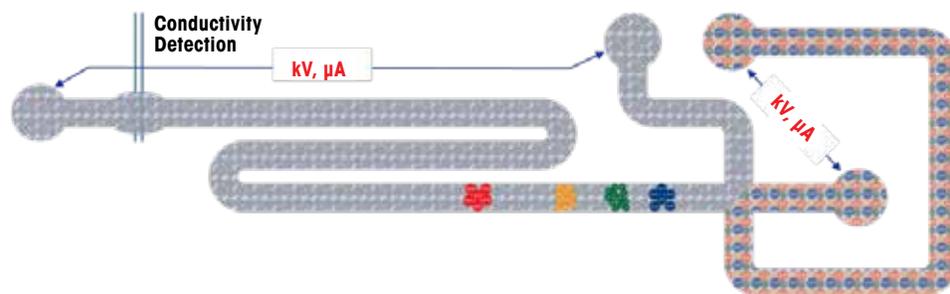
To develop a practical on-line analyzer that uses MCE technology, such as METTLER TOLEDO Thornton's 3000CS, the required high voltage electrodes and capillary must be capable of continuous operation, with sample and the



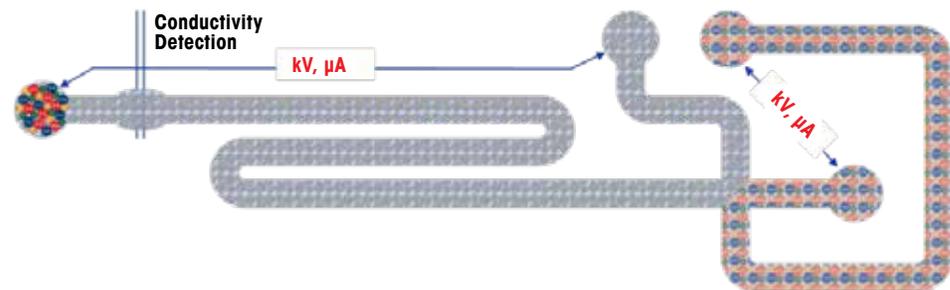
a - Voltages are controlled to draw fresh sample, standard and electrolyte into capillaries.



b - Voltage is adjusted briefly to move an aliquot of sample and internal standard ions into the separation capillary.



c - Voltage is adjusted to attract ions and separate them based on electrophoretic mobilities.



d - Measurement is completed with capillaries cleared.

Figure 5 - Steps of microfluidic capillary electrophoresis measurement

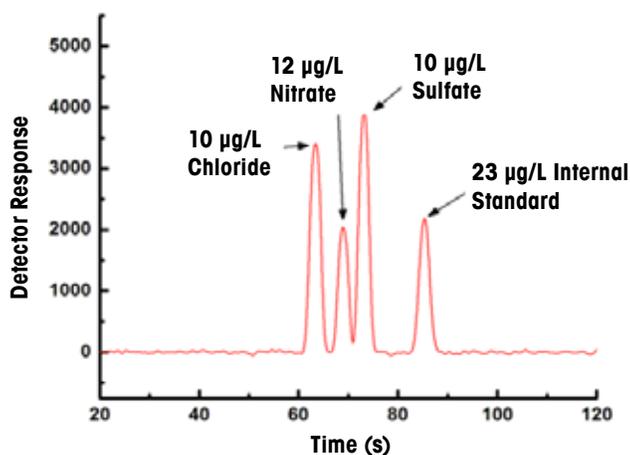


Figure 6 - The internal electropherogram is processed to obtain direct concentration readouts.

necessary electrolyte replenished with each measurement cycle. These requirements are achieved with a design using a replaceable microfluidic capillary cartridge that contains the capillaries, electrodes, solution reservoirs, and conductivity detector.

Measurement process

The incoming sample goes to an overflow chamber that maintains continuous flow so that each measurement cycle uses a fresh sample. An automatic three-way valve selects either the on-line sample or a grab sample if one is available.

The cartridge contains supply and separation capillaries that are linked together. At the beginning of each measurement cycle, precision pumps deposit sample mixed with an internal standard in the reservoirs at both ends of the supply capillary. Background buffer electrolyte is delivered to the reservoirs at both ends of the separation capillary. Voltage is then applied across the two

capillaries to pull the ions in both solutions from the reservoirs into the respective capillary sections (see Figure 5a).

The voltage is momentarily altered, causing a small aliquot of ions from the supply capillary to enter the separation capillary (see Figure 5b). Voltage continues to pull the aliquot of ions through the long separation capillary, with the highest mobility ions moving the fastest so they will reach the conductivity detector first (see Figure 5c).

The different ions in the sample always arrive at the detector in the same order, providing unambiguous identification. The voltage continues to purge all extraneous ions from the capillary, preparing it for the next measurement cycle (see Figure 5d). Conductivity peaks for each ion plus the internal standard are measured and processed to obtain the chloride and sulfate concentrations (see Figure 6). The entire preparation and measurement cycle is accomplished in 15-30 minutes.

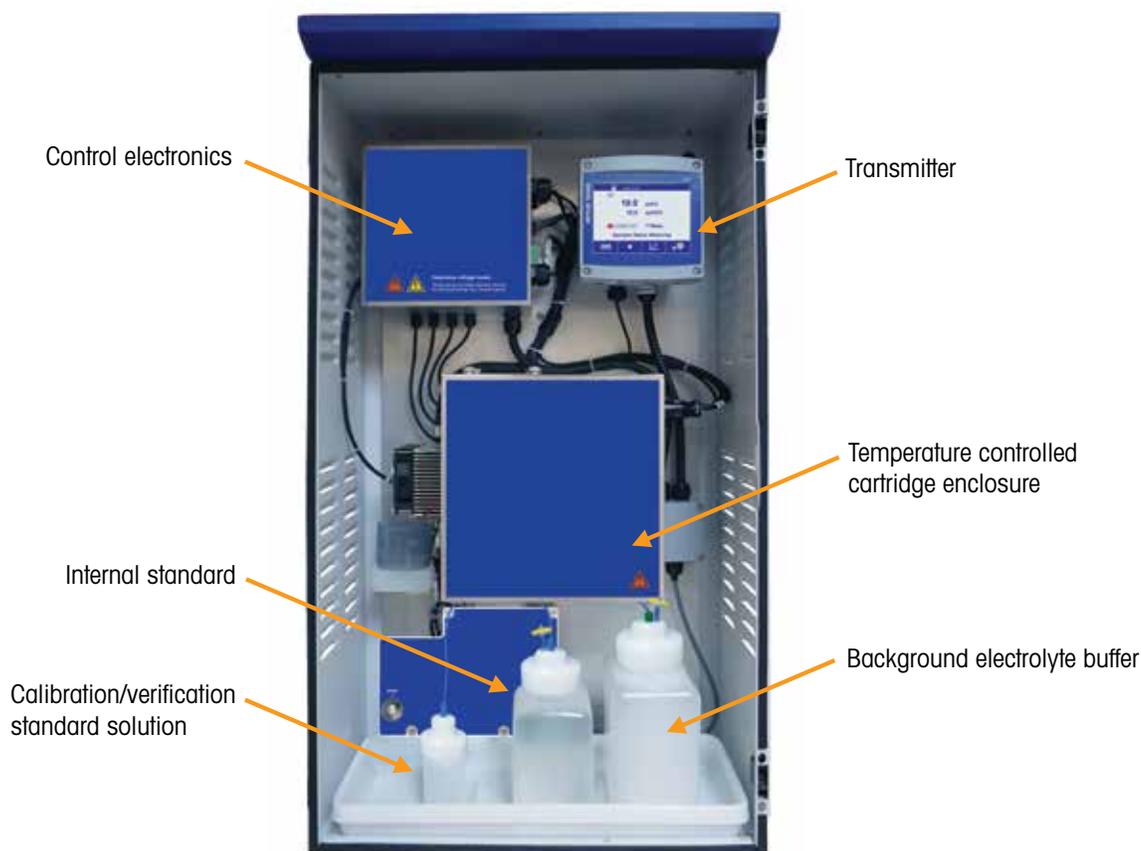
Analyzer components

The various parts of the 3000CS Analyzer are shown in Figure 7. The microfluidic capillary cartridge is the heart of this new analyzer platform and is housed in a temperature-controlled module that also provides protection around the high voltage connections. The cartridge requires replacement approximately once every two months, depending on the frequency of measurement. Reagents include the background buffer electrolyte and the internal standard solution that are used in every measurement cycle. The grab sample provision also enables

measurement of a chloride/sulfate standard solution for periodic verification or calibration.

The transmitter module displays a direct readout and trending of ppb chloride and sulfate. Its color touchscreen accesses intuitive menus for setup and operation and its predictive diagnostic features enable optimized maintenance scheduling. The transmitter includes multiple relays and output signals for alarming and retransmission of concentration data.

Figure 7 - Components of the METTLER TOLEDO Thornton 3000CS Chloride/Sulfate Analyzer



Conclusion

With chloride and sulfate being key corrosive contaminants in power plants, the need to measure their levels has increased with the rise in power plant cycling as well as construction of larger power plants with more expensive capital assets. Existing methods to monitor the levels of these contaminants have a high cost of acquisition and operation. Moreover, substitute methods, such as degassed cation conductivity, do not provide ppb-level monitoring of individual contaminants, thus reducing their effectiveness in helping control levels of each ion. Microfluidic capillary electrophoresis offers a robust on-line measurement method that is easy to use and maintain, and has a low total cost of ownership. With reliable and accurate ppb-level measurements, most high pressure and nuclear plants can attain near real-time surveillance of their feedwater or steam quality. Additional plants using amine treatment will welcome the capability to identify the more corrosive inorganic ions when less corrosive organic anions may be raising cation conductivity readings.

► www.mt.com/3000CS

References

1. Ogan, Palmer, Dekleva, "On-Line Monitoring of Chloride and Sulfate in the Steam Cycle with a New Analytical Technique, EPRI 10th International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators, Seattle, WA, June 2012.
2. Palmer, Dekleva, Heim, Ogan, "On-Line Monitoring of Chloride and Sulfate in the Steam Cycle with a New Analytical Technique," PowerPlant Chemistry 15(1), Jan/Feb 2013, pp 4-7.

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