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Evaluation of an Online Chloride and Sulfate Analyzer

Microfluidic Capillary Electrophoresis

2018 TECHNICAL REPORT

Evaluation of an Online Chloride and Sulfate Analyzer

Microfluidic Capillary Electrophoresis

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ABSTRACT

Microfluidic capillary electrophoresis (MCE) is a novel instrument concept that could provide online analysis for chloride and sulfate in water or steam at a low level (with a detection limit of <1 parts per billion [ppb]). A field demonstration of a commercially available MCE analyzer was conducted at a conventional fossil power plant to evaluate installation requirements, sample volume requirements, necessity and complexity of operator intervention, reagent consumption, analysis and calibration, and instrument accuracy in steam and boiler water samples. During the field demonstration, a condenser leak occurred, providing a unique opportunity to evaluate analyzer response to changing cycle chemistry conditions from contaminant ingress. Grab samples analyzed for chloride and sulfate with an ion chromatography unit were compared to the MCE analyzer results. Online cation conductivity measurements were compared to the calculated values using chloride and sulfate concentrations. This report presents results and conclusions from the field demonstration.

Keywords

Chloride
Ion chromatography
Microfluidic capillary electrophoresis (MCE)
Online instrumentation
Steam chemistry
Sulfate

EXECUTIVE SUMMARY

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PRIMARY AUDIENCE: Conventional fossil and combined-cycle plant chemistry users

SECONDARY AUDIENCE: Nuclear chemistry users

KEY RESEARCH QUESTION

Chloride and sulfate are critical parameters in conventional fossil and combined-cycle heat recovery steam generator plants because they can contribute to stress corrosion cracking in steam-touched boiler tubes, steam turbines, and the shell side of feedwater heaters. Low-level monitoring in steam is essential for understanding and minimizing steam turbine salt deposition. Cation or degassed cation conductivity can provide indirect measurement of these ions but is incapable of specific low-level indication to ensure meeting the recommended steam limits of 2 ppb, respectively. Online ion chromatography is a high-cost, labor-intensive method and thus not a good fit in modern conventional fossil or combined-cycle plants. A novel online analyzer using microfluidic capillary electrophoresis (MCE) in the test phase may provide accurate, low-level online analysis for chloride and sulfate.

RESEARCH OVERVIEW

A field demonstration of the MCE analyzer was conducted on a conventional fossil unit with a 2850 psig (19.65 MPa/196.5 bar) drum boiler. The analyzer was installed in the plant chemistry sampling and conditioning room, and boiler water and main steam samples were analyzed for a ~6-month period.

KEY FINDINGS

- Operator intervention was observed to be roughly equivalent to other commonly used online chemistry analyzers in power plants. At a one sample per hour frequency setting, the reagents lasted 78 days. The analyzer utilized a disposable cartridge that had to be replaced after 3 months, which was in line with the manufacturer’s expected useful life of 2–3 months. The cartridge replacement and reagent change-out required approximately 30 minutes to perform.
- New cartridges ship precalibrated, and during calibration of the new cartridge, the sulfate did not rinse to <5 ppb as expected with ultrapure water. On-site calibration was performed to bring the readings down to the expected levels.
- Calibration with 5 ppb and 25 ppb standards was straightforward, and the analyzer rinsed down without issues for return to normal service.
- Internal sample tubing replacement is a complex task, and a service visit from the manufacturer is recommended.
- The online analyzer correlated closely to grab sample results analyzed in a lab using ion chromatography. In addition, during the demonstration cation conductivity was calculated using the analyzer readings and correlated closely to the unit’s online cation conductivity readings.

- Proper shutdown and storage per the manufacturer's operating manual were found to be critical to successful operation. An extended idle period resulted in the introduction of air into the cartridge, which affected the analyzer operation and required a time-consuming effort to resolve.
- An upstream filter was used to remove suspended solids in the sample to minimize plugging of the sample tubing. A cation resin cartridge was installed to remove ammonia to avoid interference with ion separation.
- A "clean" power supply was required, to provide a constant voltage.

WHY THIS MATTERS

Power plant chemistry users may benefit from the evaluation in consideration for incorporating this technology into their cycle chemistry monitoring program for an existing asset or new power plant construction. Online measurement of steam samples may ensure that the unit achieves the recommended steam purity of < 2 ppb and would allow prompt response to contaminant ingress.

HOW TO APPLY RESULTS

Power plant cycle chemistry users may find the evaluation valuable in determining how to enhance their current monitoring program. During this evaluation, the equipment manufacturer made improvements to the analyzer design, functionality, and user-interface features. Additional testing should be conducted to determine how film-forming products may impact the analyzer.

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1
INTRODUCTION

Chloride and sulfate are critical parameters in conventional fossil and combined-cycle heat recovery steam generator plants because they can contribute to stress corrosion cracking in steam-touched boiler tubes, steam turbines, and the shell side of feedwater heaters. In addition, they are precursors to underdeposit corrosion from hydrogen damage in boilers and high-pressure (HP) evaporator tubes. Modeling conducted in previous EPRI research showed potential for sodium chloride deposition in low-pressure (LP) steam turbines at concentrations <1 ppb [1]. Low-level monitoring for chloride and sulfate in steam is essential for understanding and minimizing steam turbine salt deposition, but low-level detection is challenging. Cation or degassed cation conductivity may be used as an indirect measure of these ions. However, degassed cation conductivity is not effective in the presence of breakdown products, formate and acetate, from neutralizing amines that may be used to control pH or other organic constituents that may result in elevated conductivity. Traditional techniques involve obtaining grab samples of the condensate or steam and performing the analysis by ion chromatography (IC) in the plant or corporate chemistry laboratory or in a commercial laboratory. The process of grabbing a sample, transporting the sample to the laboratory, injecting an aliquot for the analysis, and waiting for the results is time consuming, and it introduces potential sample contamination from sample handling. Online IC has been used by some fossil plants and many nuclear plants. In some cases, the use of the online technology was abandoned due to the labor required to operate and maintain the instrument.

Principle of Microfluidic Capillary Electrophoresis

Capillary electrophoresis uses an electric field to separate ions in an electrolyte based on their mobilities, as shown in Figure 1-1. Capillary electrophoresis has similarities to IC for separating ions in a sample, but also there are 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 using an eluent carrier. The anion column must be periodically regenerated, and the system often has a resin guard column. Electrophoresis, on the other hand, uses differences in electrophoretic mobility to separate the ions as they are attracted through a capillary by high-voltage direct current.

It is primarily the ions that are attracted through the capillary, and not the bulk sample, so particles (such as iron oxides) are less of a concern with electrophoresis as compared with IC. The ions eventually pass a conductivity detector near the end of the capillary, where the response is used to generate an electropherogram, like an ion chromatogram. Quantification is based on the conductivity detector compared to an internal reference or calibration standard.

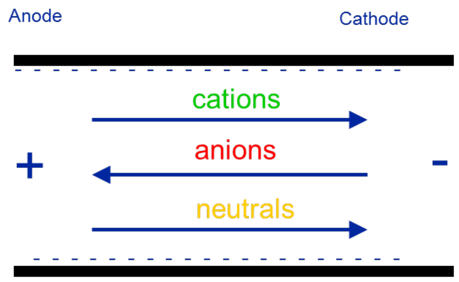


Figure 1-1
Capillary electrophoresis concept

MCE Instrument Concept

Previous research on microfluidic capillary electrophoresis (MCE) was initiated at Colorado State University and subsequently developed further for power plant cycle chemistry measurements at Advanced Microlabs [2, 3]. To develop practical online instrumentation using MCE technology, the high-voltage electrodes and capillary must be capable of continuous operation, with sample and electrolyte replenished for each measurement cycle. These requirements are achieved with a design using a replaceable microfluidic capillary cartridge that provides fresh electrodes, clean capillary, and clean solution reservoirs [4]. The cartridge and steps of its operation are shown in Figures 1-2 through 1-5.

The incoming sample goes to an overflow chamber that maintains continuous flow so that each measurement cycle has a fresh sample. An automatic 3-way valve selects either the online sample or a grab sample. At the beginning of each measurement cycle, precision pumps deliver sample mixed with internal standard to the reservoir at the charged end of the supply capillary shown in Figure 1-2. Background buffer electrolyte is delivered to the reservoirs at both ends of the separation capillary and the other end of the supply capillary. Voltage is then applied across the capillaries to drive the ions of each solution from the reservoirs through the respective capillary sections as shown in Figure 1-1 [4].

The voltage is momentarily altered to cause a small aliquot of ions from the supply capillary to enter the separation capillary as shown in Figure 1-3. Voltage continues to drive the aliquot of ions through the long separation path, with the highest mobility ions moving the fastest, so they will reach the conductivity detector first as in Figure 1-4 [4].

The various types of ions always arrive at the detector in the same order, enabling 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 as illustrated in Figure 1-5. Conductivity peaks for each ion, including the internal standard, are measured and processed to obtain the chloride and sulfate concentrations as shown in Figure 1-6. The display, alarms, and outputs are updated and held at the new measured values with each cycle. The entire preparation and measurement cycle is accomplished in 15 minutes [4].

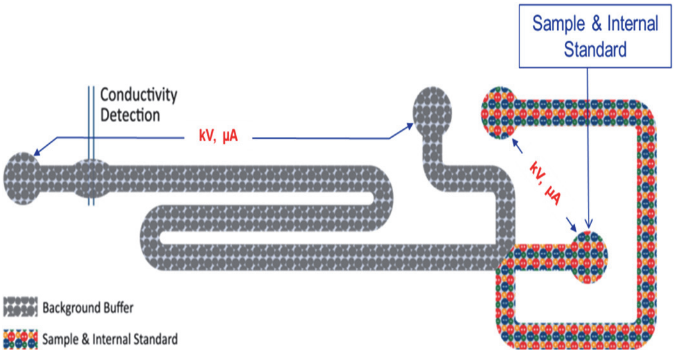


Figure 1-2
Sample loading

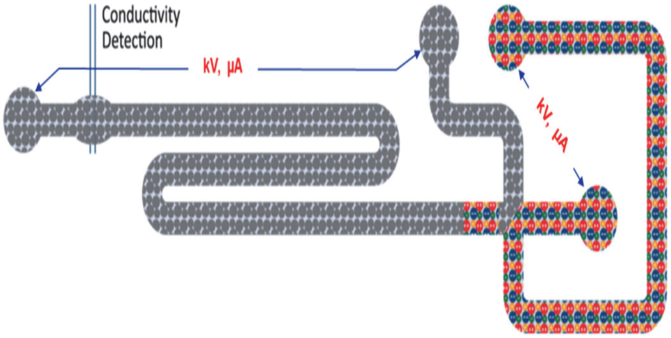


Figure 1-3
Introduction of sample into separation capillary

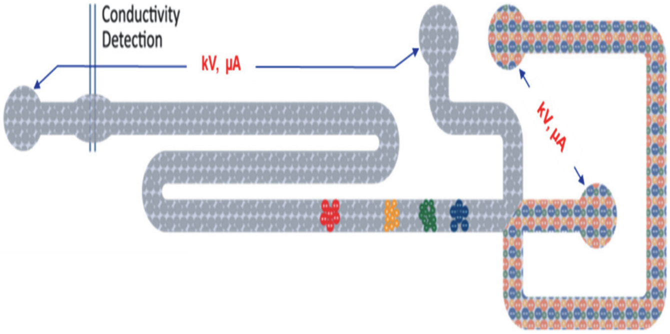


Figure 1-4
Ion separation

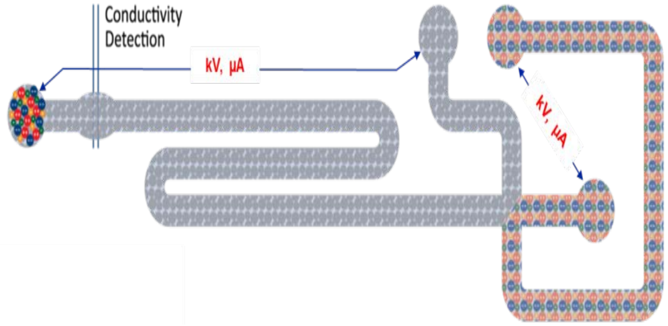
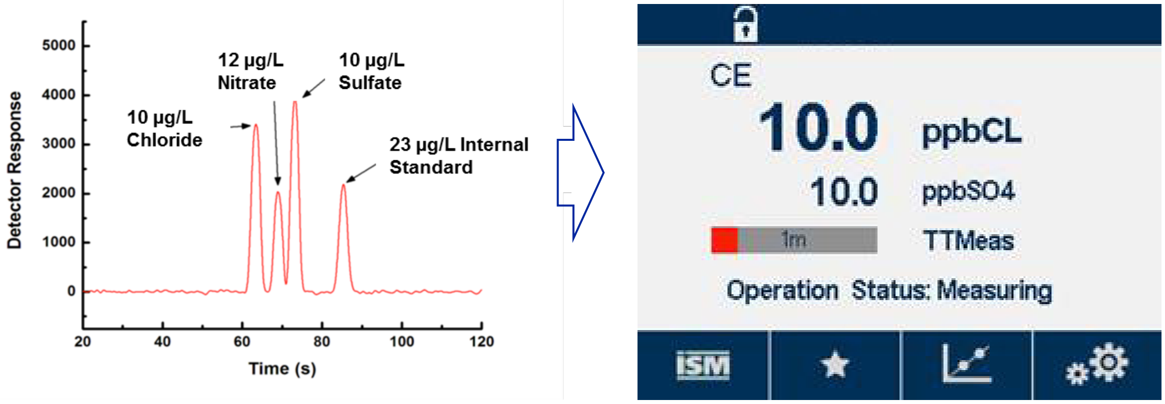


Figure 1-5
Measurement



CE
10.0 ppbCL
10.0 ppbSO4
1m TTMeas
Operation Status: Measuring

Figure 1-6
Internal electropherogram processed to obtain direct concentration readout

The various parts of the MCE analyzer for chloride and sulfate analysis are shown in Figure 1-7. The microfluidic capillary cartridge is the heart of the analyzer platform and is housed in a temperature-controlled module that also provides protection around the high-voltage connections. 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. The grab sample provision also enables measurement of a chloride/sulfate standard solution for periodic verification or calibration [4].

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 output signals for alarming and retransmission of concentration data [4].

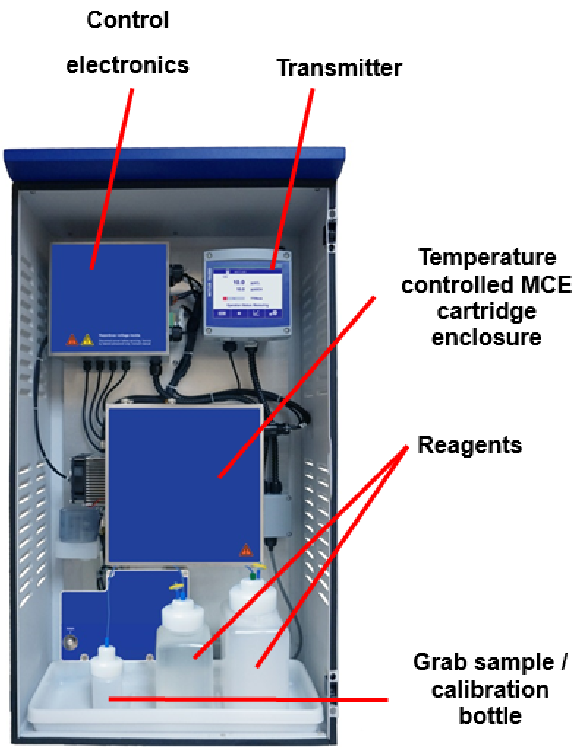


Figure 1-7
Components of the Mettler Toledo chloride and sulfate analyzer (MCE)

2

FIELD DEMONSTRATION

Description and Results

A field demonstration was conducted by EPRI at Ameren's Labadie Station in Missouri from July 2017 through February 2018. Main steam and boiler water were analyzed with the online MCE analyzer on all four Labadie units. The plant has four subcritical drum units operated at 2850 psi (19.65 MPa/196.5 bar) with a total capacity of 2380 MW and started operating in 1970. The feedwater treatment is all volatile treatment oxidizing (AVT(O)), and boiler treatment uses trisodium phosphate (TSP). The condenser uses once-through cooling water, and the units are not equipped with condensate polishers. The units have experienced frequent low-level condenser leaks, which would be reflected in the analytical measurements.

The online MCE technology has also been tested in two electric power generating nuclear light water reactors in 2016 [4,5]. Some technology advancement was made as a result of those field demonstrations and changes to the software for measuring sulfate. Advancements were related to a chloride spike, which was observed during the flush cycle. Formate was suspected after the internal standard peak, leading to misidentification of the internal standard peak. Due to the misidentification of the internal standard peak, the instrument mislabeled and misquantified identified peaks. This issue was corrected by adjusting the end time on the electropherogram to make the known internal standard peak be identified last, consistent with the method. After calibration, a mixed verification standard containing 5 ppb chloride and sulfate was prepared by the lab. All results were within 10% of the known concentration, indicating acceptable performance. Additional standards were analyzed daily during the initial week of the demonstration and following a cartridge replacement, all with acceptable results within 10% of the 5 ppb and 25 ppb mixed verification standards [4].

The objective of the Labadie demonstration was to evaluate the ability of the analyzer to measure accurately over a wide range of chloride and sulfate concentrations, perform reliably at various sample locations, provide results for comparison to grab sample analyses by ion chromatography, and enable comparison to online cation conductivity measurements. The specific goals identified for the test were:

- Evaluate measurement accuracy and instrument reliability
- Capture cation conductivity measurements to compare with chloride and sulfate concentrations and calculated cation conductivity
- Compare readings to grab samples measured on ion chromatograph

- Analyze performance of analyzer in low ppb (steam) as well as high ppb measurements (boiler water)
- Evaluate ease of replacement of consumables, by having plant personnel replace the consumables at end of life
- Identify special requirements for sample conditioning

The analyzer was set up in the Labadie chemistry lab, monitoring all four units at the plant. A 0.25-inch (3.175-cm) sample line from each unit was routed to the analyzer with individual isolation valves as shown in Figure 2-1. Per manufacturer guidance, the analyzer setup for the demonstration included a pressure relief valve set at 25 psi. A weak acid resin cartridge and a magnetic trap were mounted at the sample inlet to the analyzer, to ensure no physical interference from concentration of ammonia in the MCE cartridge or sample tubing blockage due to suspended metals. Analog outputs were connected to the data collection system, and data were collected using the plant's process computer data historian system. Regulated 120-volt alternating current (VAC) power was provided to the analyzer, to ensure minimal fluctuation in voltage, which could disturb the measurement cycle.

Figure 2-1
Chloride and sulfate analyzer setup in the Labadie chemistry lab

The evaluation was planned to run in three phases: main steam of all units, boiler water of all units, and a repeat of main steam. Deionized water was measured by the analyzer for four days between the boiler water and repeated main steam measurement phases to ensure that the analyzer was rinsed out to avoid cross-contamination from the higher-concentration boiler water measurement. The measurement cycle time was set at 45 minutes, with the plant process computer data historian system capturing data every 20 minutes. The analyzer output was scaled to read from 0 to 200 ppb for both chloride and sulfate.

The analyzer commenced Phase 1 measurements of chloride and sulfate on main steam samples from July 14, 2017, to August 4, 2017. The main steam sample from each unit was measured for approximately 7 days each. In addition to online chloride and sulfate measurements, cation conductivity and sodium data were also collected, as per the normal plant monitoring procedures. The data, as shown in Figure 2-2, demonstrate the main steam sample characteristics in terms of all these parameters. The plant also collected grab samples periodically and sent them to an external laboratory for analysis via IC. The laboratory provided a limit of detection of 1 ppb for both ions in their testing method. The test results from various such grab samples in Phase 1 are shown in Table 2-1. The IC had a detection limit of 1 ppb. Cation conductivity was calculated based on the MCE online analysis and compared to main steam cation conductivity. Data shown in Figure 2-3 demonstrate consistent agreement, with an average offset of 0.078 µS/cm. It is suspected that this offset is caused by carbon dioxide, acetate, and/or formate ions impacting the measured cation conductivity. A benefit of the MCE analyzer is that it provides actual values for chloride and sulfate and is not influenced by these other anions that increase cation conductivity.

Analysis of the data from Figure 2-2 and Table 2-1 indicated that sodium excursions do not always result in corresponding chloride or sulfate increases and vice versa. This is in line with the difference in known carryover mechanisms (liquid or gas phase) for these ions. Also, the chloride and sulfate analyzer measured at sub-ppb levels accurately and reliably, as the online measurements were within accuracy specifications of ion chromatography readings from grab samples.

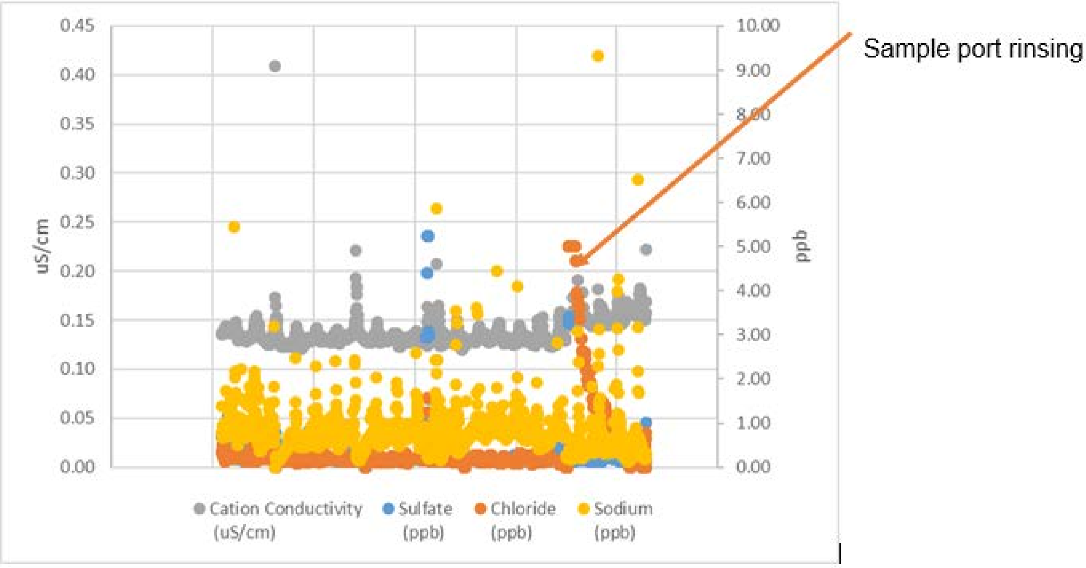


Figure 2-2
Labadie main steam measurements during Phase 1

Table 2-1
Comparison of Labadie main steam samples using MCE and IC during Phase 1

Date	Online 3000CS (ppb)		IC (ppb)	
	Chloride	Sulfate	Chloride	Sulfate
July 21, 2017	0.2	0.1	1.2	<1.0
July 24, 2017	1.3	4.4	1.5	4.0
August 4, 2017	0.8	0.1	<1.0	<1.0

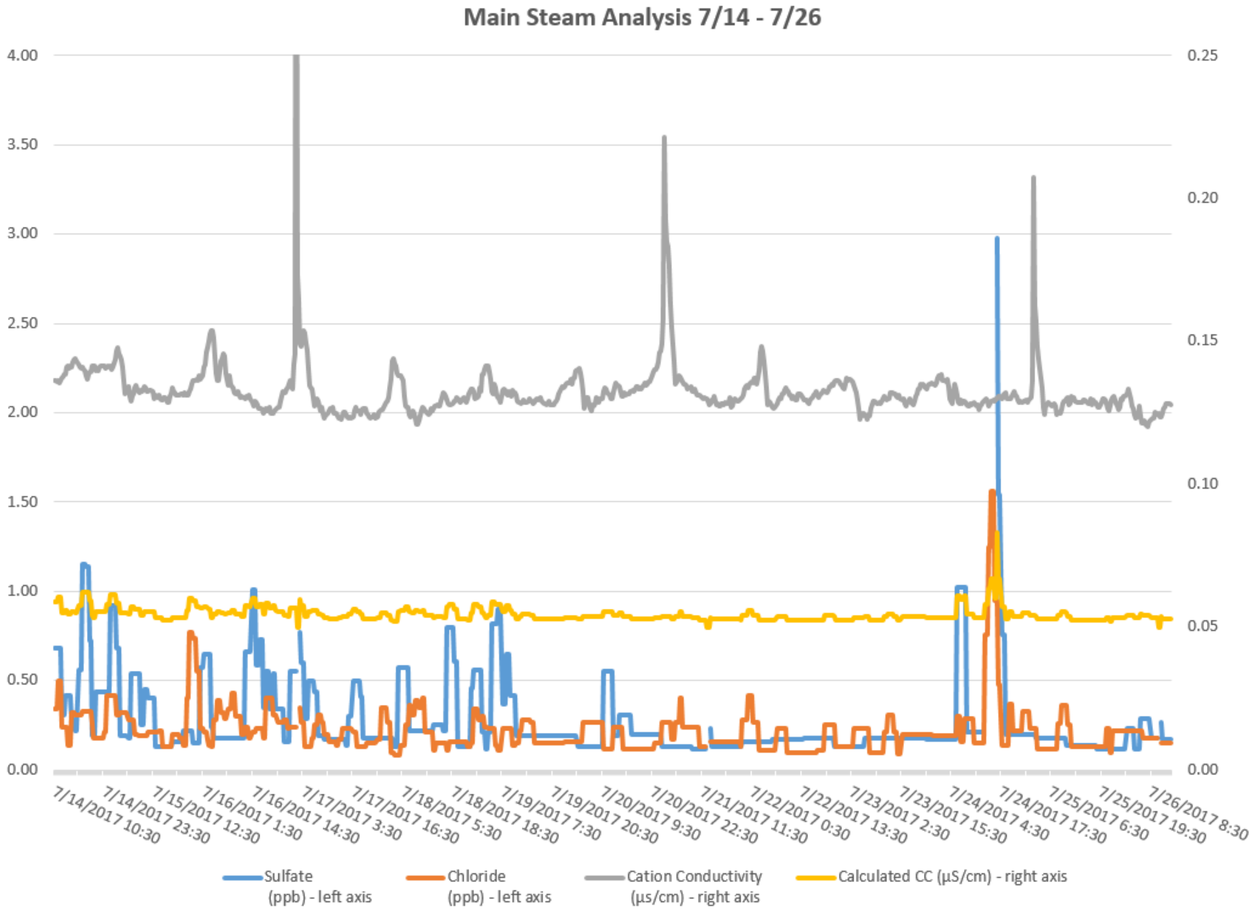


Figure 2-3
Cation conductivity on Unit 1 main steam

Labadie boiler water was sampled online for chloride and sulfate using the MCE analyzer from August 4, 2017, to September 14, 2017 (Phase 2). The boiler water sample from each unit was measured for approximately 10 days each. In addition to the MCE chloride and sulfate analysis, cation conductivity, phosphate, phosphate corrected cation conductivity, and silica were analyzed with online plant instrumentation. Figure 2-4 shows the chloride, sulfate, and cation conductivity values for the boiler water samples during this phase.

With disturbances in the plant, the sulfate and chloride measurements shown in Figure 2-4 are seen to fluctuate widely. The chloride and sulfate measurements show a maximum value of 200 ppb in such disturbances since the analog outputs had been scaled at 0–200 ppb during setup, which resulted in all values higher than 200 ppb being reported at a maximum of 200 ppb. In addition, when either sulfate or chloride was off-scale, the other value also went off-scale.

To ensure continued performance in very high ppb sample waters, the MCE reagents were modified and data processing updated on the analyzer on August 21, 2017, to allow a larger range of measurement (0–500 ppb) and also to calculate the chloride and sulfate concentration independently. However, calibration could not be conducted due to contamination of calibration standards, leading to readings not fully correlating to grab sample readings. The plant collected grab samples periodically and sent them to an external laboratory for analysis via ion chromatography. As mentioned earlier, the laboratory provided a limit of detection of 1 ppb for both ions in their testing method. The test results from various such grab samples in Phase 2 are shown in Table 2-2.

Analysis of the data from Figure 2-4 and Table 2-2 indicated that the MCE analyzer responded quickly to sulfate and chloride excursions in the sample water and returned to normal as soon as the plant operations returned to normal operating conditions. Calibration of the analyzer is essential in getting accurate measurements on an ongoing basis. In the absence of a good calibration, the analyzer reading can be used for trending, with measurements close to the actual condition in the sample water. Improvements in the data processing allowed the analyzer to continue reporting measurements on a lower-level concentration of one ion even when the concentration of the other ion was out of range on the analog output (see data for measurement on September 6 in Table 2-2).

Figure 2-4
Labadie boiler water measurements during Phase 2

Table 2-2
Comparison of Labadie boiler water samples using MCE and IC during Phase 2

Date	Online 3000CS (ppb)		IC (ppb)	
	Chloride	Sulfate	Chloride	Sulfate
August 8, 2017	13	80	9.4	67
August 11, 2017	13	74	9.1	65
August 14, 2017	207	207	71.9	477
August 14, 2017	207	207	33.9	246
August 31, 2017	25	106	18.5	83.1
September 6, 2017	34	207	30.4	174
September 8, 2017	6	46	2.5	20.7

Finally, the MCE analyzer was reconnected and measured chloride and sulfate from main steam samples from September 16, 2017, to October 19, 2017, and from December 15, 2017, to January 24, 2018 (Phase 3). From September 16 to October 19, main steam was measured online for approximately 7 days on each of the four units, and cation conductivity and sodium data were collected in addition to chloride and sulfate. On October 19, the reagents were consumed and the trial was paused. On December 15, plant chemical testers changed out the reagents and the trial was resumed until January 24, 2018.

Phase 3 data are shown in Figure 2-5. The high levels of various ions and conductivity at the earlier part of Phase 3 (circled in Figure 2-5) were due to a plant restart after plugging of leaking condenser tubes. The plant collected grab samples periodically and sent them to an outside laboratory for analysis via IC. The test results from various grab samples in Phase 3 are shown in Table 2-3.

In general, the analyzer responded quickly to contamination and rinsed down rapidly to give accurate and reliable low-level measurements after each such contamination event was resolved. In general, the online measurements with the analyzer correlate with grab sample measurements within their levels of accuracy. The discrepancies seen in Figure 2-5 are suspected to be due to contamination during grab sampling and handling.

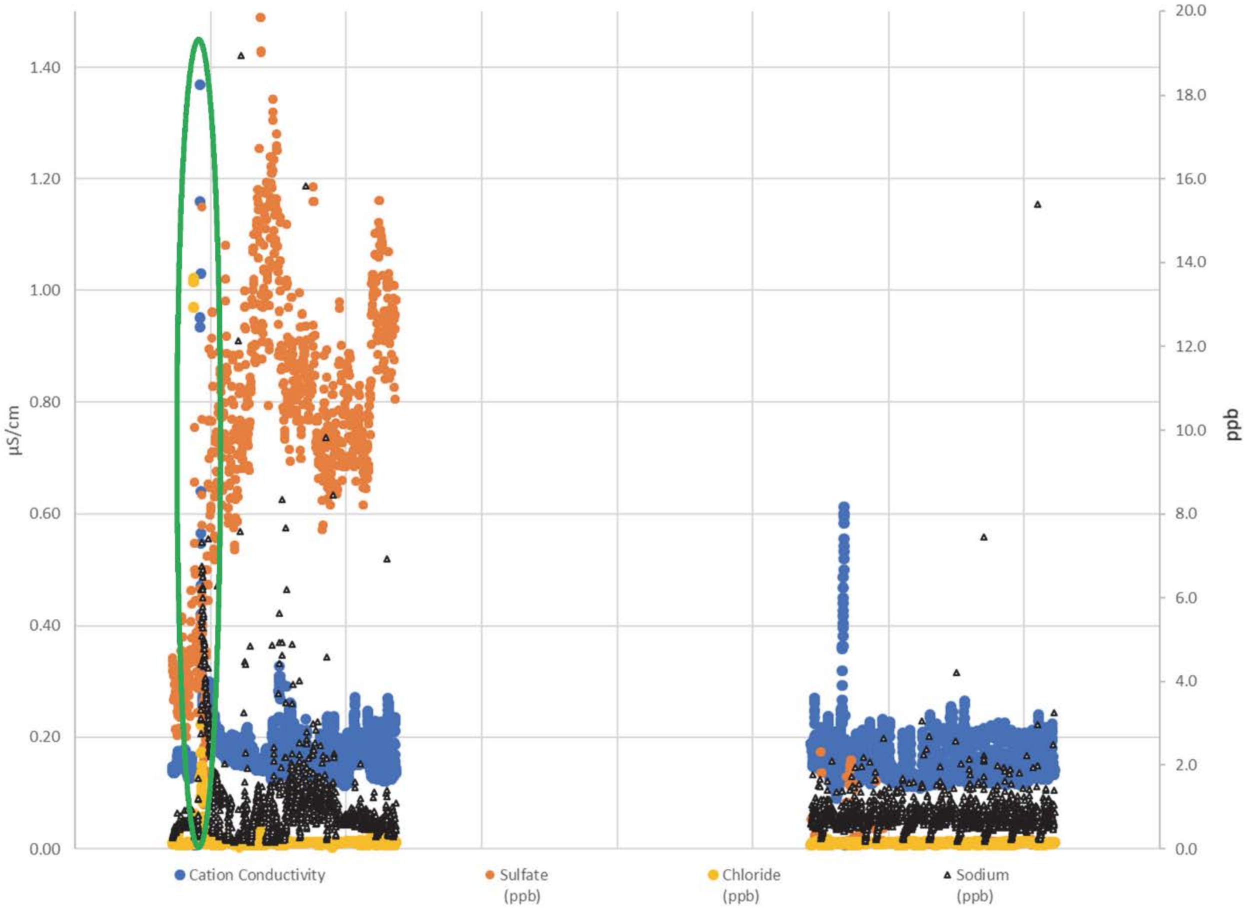


Figure 2-5
Labadie main steam measurements during Phase 3

Table 2-3
Comparison of Labadie main steam samples using MCE and IC during Phase 3

Date	Online 3000CS (ppb)		IC (ppb)	
	Chloride	**Sulfate**	**Chloride**	**Sulfate**
September 21, 2017	0.12	5.95	<0.5	12
September 26, 2017	0.15	9.85	<0.5	10
September 29, 2017	0.22	11.7	1.7	11
October 10, 2017	0.13	9.92	2.1	10

Plant Observations on Operation and Maintenance of the Analyzer

As discussed earlier, an issue with maximum scale was encountered. If either chloride or sulfate read max scale (200 ppb), both readings report at max scale. The manufacturer has increased this to 300 ppb of chloride or sulfate, with plans to extend the maximum range up to 500 ppb.

Proper shutdown and storage were found to be important, and a long idle period caused an issue with air getting into the new cartridge. The analyzer manual provides detailed layup and storage instructions, which depend on duration of shutdown expected. Cartridge and reagent replacement required approximately 30 minutes to perform. The new cartridges ship precalibrated, but it was found that the sulfate readings were higher than expected with the new cartridge. The analyzer should rinse to < 5 ppb chloride and sulfate with ultrapure water but stayed at ~8 ppb. Calibration brought values down to expected levels and was run for the next month without any related issues. Routine calibrations are performed with 5 ppb and 25 ppb standards and then rinsed down. This was found to be a straightforward process, and no issues were experienced.

Installation requirements include a regulated 120-VAC power supply. A 0.25-inch sample line, with sample pressure at 5–100 psi, supplied the requisite 50-mL/min flow rate. Setup also includes a pressure relief valve set at 25 psi. A weak acid cation exchange column to ensure ammonia < 5 mg/L was supplied. A magnetic filter on the sample inlet was used to limit the amount of iron to the analyzer. The analyzer also requires an open drain with no backpressure. Lastly, the analyzer has two analog outputs and several relays available for data collection, remote monitoring, and alarming in the plant distributed control system or programmable logic controller (PLC).

Following the field demonstration, the MCE analyzer was purchased by Ameren and relocated to the Sioux Plant, which consists of two supercritical units. On-site calibration has not been needed, and results for a new cartridge are generally within the allowable range on the 5 ppb standard check. Air bubble entrainment in one of the reagents being delivered to the cartridge caused some issues but was corrected after an on-site service visit from the manufacturer. This problem has not reoccurred. Another minor issue was experienced with one of the electrical contacts failing to contact the cartridge, resulting in no analysis due to a “no cartridge detected” error. This was corrected by cleaning the contact, and the problem has not reoccurred. Lastly, at the Sioux Plant, a chemistry excursion occurred during which the cation conductivity increased in the steam and subsequently in the condensate. The MCE analyzer did not indicate elevated chloride and sulfate, as confirmed by grab samples analyzed by IC the next day, and the unit remained in service. Without the new analyzer it is likely the unit would have been shut down based on elevated cation conductivity.

3

SUMMARY AND CONCLUSIONS

Field Demonstration Highlights

A field demonstration of an MCE unit for low-level chloride and sulfate online analysis was conducted on a conventional fossil drum boiler to evaluate the following analyzer parameters:

- Sample and installation requirements
- Necessity and complexity of operator intervention
- Reagent consumption
- Analysis and calibration
- Instrument accuracy

A condenser leak occurred during the test, which provided an opportunity to evaluate the analyzer under changing chemistry conditions. In summary, the MCE chloride and sulfate analyzer performed reliably through the 6-month test period after an issue related to maximum scale was resolved.

For optimal installation, a regulated 120-VAC power supply should be utilized. In the field demonstration, the MCE analyzer manufacturer's support was utilized to identify the best supply circuit. A 1¼-inch (3.175-cm) diameter sample line at sample pressure 5–100 psi was used to deliver approximately 50 mL/min to the analyzer. An open drain with no backpressure was also provided. Per manufacturer guidance, the analyzer setup for the demonstration included a pressure relief valve set at 25 psi and a weak acid cation exchange column to ensure ammonia is less than 5 mg/L. A magnetic trap filter on the sample inlet for minimizing iron going to the analyzer is optional. The need for this filter depends on the amount of iron in the sample being analyzed, and it was not used for this demonstration. The analyzer has two outputs, and both were connected to the host plant digital control system (DCS) for data acquisition.

In general, operator intervention needs were observed to be roughly equivalent to those of other commonly used online analyzers in fossil power plants, such as ones used for silica, sodium, and hydrazine. During this test, a one sample per hour frequency setting allowed the reagents to last 78 days. In addition to reagents, the analyzer utilizes a disposable cartridge that has an expected useful life of 2–3 months. The cartridge replacement and reagent change-out took approximately 30 minutes to perform. Other consumables include sample tubing internal to the analyzer, and replacement of this tubing appeared to be a complex task. Scheduling a service visit from the analyzer manufacturer may be a necessary option for tubing replacement in some applications.

Calibration with 5 ppb and 25 ppb standards was straightforward, and the analyzer rinsed down without issues for a return to normal service. New cartridges ship precalibrated, but during calibration of the new cartridge during this demonstration, the sulfate did not rinse to <5 ppb as expected with ultrapure (0.055 µS/cm) water at 25°C. An on-site calibration was performed and brought the readings down to expected levels.

Proper shutdown and storage were found to be critical to successful operation. Idle periods can result in the introduction of air into the disposable cartridge. Air intrusion to the cartridge affects the analyzer operation and required a time-consuming resolution. Ultimately the cartridge was replaced, which could be a costly event for end-users.

From an accuracy perspective, results from the online analyzer correlated closely to grab sample results analyzed in a lab using ion chromatography. Also, during the demonstration, cation conductivity was calculated using the analyzer readings, and the results correlated closely to the results obtained from the unit’s online cation conductivity analyzers.

Plant Application

Ameren purchased an analyzer, and it was relocated to the Sioux Plant, which consists of supercritical units. The analyzer was connected to the steam samples. Shortly after installation the steam cation conductivity increased to an alarm level. The steam purity was in action level 3 and would have required the unit to be removed from service. The online chloride/sulfate analyzer indicated that the concentrations were within normal operating specifications, so the unit was not shut down. Grab samples collected during the excursion and analyzed by IC the next day confirmed the online analyzer results and validated the decision to keep the unit online. The excursion resulted from some type of organic contamination as confirmed by total organic carbon (TOC) grab sample analysis. The online analyzer provided real values for chloride and sulfate and not the inferred poor steam purity from online cation conductivity measurements, thereby showing its practical value.

Further Research

Film-forming products are being utilized in a number of conventional fossil and combined-cycle plants. It is not known whether filming products or filming amines would influence the ability of the analyzer to accurately quantify low-level chloride and sulfate concentrations. The following additional laboratory testing is suggested:

- Revise the current method to measure acetate and formate
- Determine possible interferences from film-forming products
- Evaluate and quantify the interference from neutralizing amines and the requirement for a cation guard column

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