Analysis of anions in power plant waters using capillary electrophoresis

Application Note

Power Generating Industry

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Abstract

Power plant circuit waters must be ultrapure and treated to minimize corrosion. Additives are ammonia and/or morpholine (pH control), and hydrazine (powerful reducing agent). Corrosion products, consisting mainly of insoluble metal species, build up deposits in the tubings where trace ionic contaminants from the feedwater can concentrate resulting in a highly corrosive local environment. Low levels of small anions and cations must therefore be monitored in order to minimize operational costs and contribute to the safe operation of the plant. Low ppb levels of small inorganic and organic anions are analyzed fast and reliably by capillary electrophoresis (CE) using indirect UV detection.

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Experimental and results

Anion analysis was performed using the Agilent Capillary Electrophoresis system equipped with DAD detection and computer control via Agilent ChemStation. The method is based on the Agilent Inorganic Anion Solutions Kit (part number 5063-6511). A bubble cell capillary was used to increase detection limits. Additionally, the capillary effective length was reduced to 50 cm to shorten analysis times without sacrificing resolution between nitrate and oxalate. All vials (glass vials for buffer, polypropylene vials for samples) and clear olefine vial caps were washed overnight with deionized water (Milli-Q Plus or comparable quality) to eliminate contamination. Deionized water was also used to prepare the anion standards daily. Gluconic acid [10 mM] was added to all standards and samples to decrease carbonation.

New capillaries were subjected to a conditioning procedure: 10 minutes flush 1 N NaOH, 3 minutes flush 0.1 N NaOH, dip inlet/outlet in water, 15/30 minutes flush from two different buffer vials. Each flush step used its own waste vial. Afterwards, 10 standard runs injecting hydrodynamically from a 100 ppb standard solution in water were performed thereby equilibrating the capillary.

Prior to each analytical run a preconditioning procedure together with automatic buffer vial replenishment was performed to keep migration times stable. This procedure and more details are found in the caption of figure 1, which shows the analysis of anions in reconstituted secondary circuit water matrix.

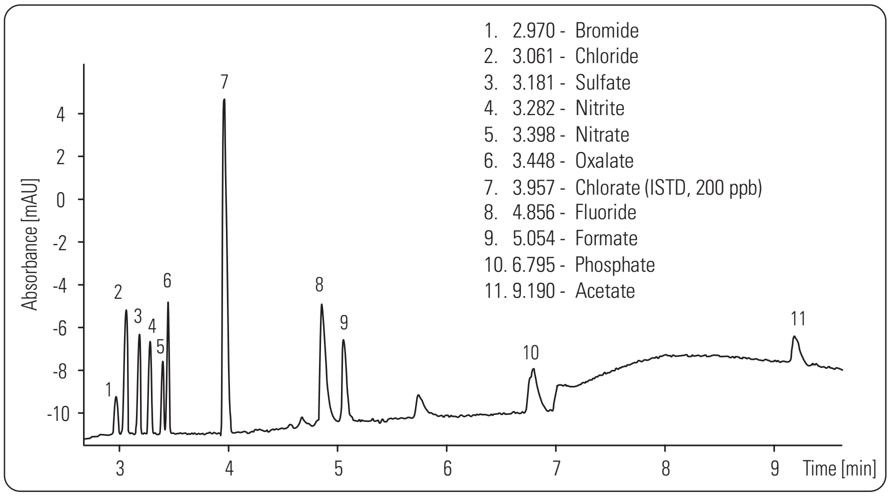

Figure 1
The analysis of anions in reconstituted secondary circuit water matrix.

Chromatographic conditions

Sample:	20 ppb anions in matrix, (5 ppm morpholine, 50 ppb hydrazine, 300 ppb ammonia, 300 ppb methylamine, 5 ppm borate)
Injection:	-5 kV x 20 sec
Capillary:	length = 58.5 cm, effective length = 50 cm; 50 µgm id, BF3
Buffer:	inorganic anion buffer
Temperature:	30 °C
Voltage:	30 k, negative polarity
Detection:	signal 350/50, reference 245/10
Precondition:	flush 2 min 0.1 N NaOH, dip both ends in water, flush 2 x 2 min with electrolyte

The assay was linear over the range 10–30 ppb ($r^2 > 0.98$) with a detection limit of 1-5 ppb. This was sufficient for reliable determination of ion concentrations normally found in circuit water samples. Repeatability (n = 6, with internal standard) was 0.08 - 0.19 % RSD for migration times and 2.68–5.63 % RSD for corrected peak areas (except for acetate, 10.44 % RSD). This excellent migration time repeatability was achieved even in the presence of a complex sample matrix. The repeatability of peak areas was sufficient for reliable quantitation.

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