Analysis of sulfur anions in Kraft liquors using capillary electrophoresis

Application Note

Chemical Analysis

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Abstract

The proper function of Kraft recovery furnaces is a very important part of the chemical recovery process at a Kraft pulp mill. In the recovery furnace sulfur anions, such as sulfate in the black liquor are converted to sulfide anions in the green liquor. Sulfide anions in the pulping reactions produce stronger paper and if its concentration is too low, the paper produced loses its strength. If the sulfide concentration is very high, polluting emissions from the Kraft recovery furnaces are increased. Wet chemical tests and ion chromatography (IC) have traditionally been used to analyze process liquors. CE is a worthy replacement for IC due to less buffer consumption, less maintenance, and considerably shorter run times.

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Experimental and results

In the pulp and paper industry Kraft liquors must be monitored for the anion content both to monitor the quality of the liquors and for environmental reasons. CE is used to measure sulfur anions (sulfide, sulfate, thiosulfate and sulfite), chloride anions and oxalate anions. Wet chemical tests are used for hydroxide, carbonate, sulfide and sulfate anions. The sulfate and sulfide anions are used to calculate the percent reduction of the green and white liquor, which is one measure of the efficiency of the recovery furnace. Control personnel uses the results of the tests to adjust process control parameters that influence the degree of conversion of sulfur containing anions to sulfide anions.

CE is also used to measure the amount of chloride ions in Kraft recovery process liquors. Chloride concentrations tend to build up in the recovery process to an equilibrium level depending on inputs to the system. High chloride concentration can be detrimental because it increases the rate of corrosion for some type of metals.

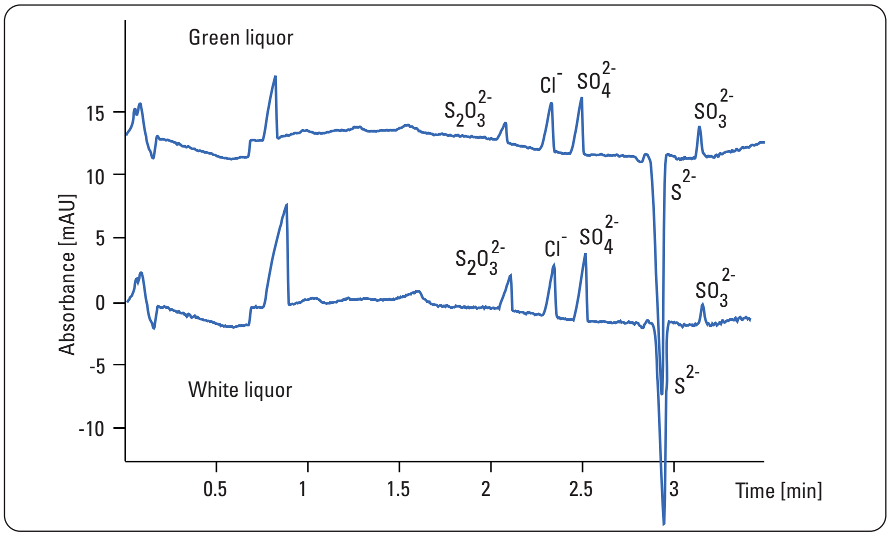

Figure 1
Analysis of green and white Kraft liquors.

Chromatographic conditions

Sample:	green and white Kraft liquor
Injection:	1 sec @ 50 mbar sample, dip inlet in water, 2 sec @ 50 mbar buffer
Capillary:	effective length 24.5 cm, total length 33 cm, internal diameter 50 µm
Buffer:	2.25 mM pyromellitic acid, 6.5 mM sodium hydroxide, 0.75 mM hexamethonium hydroxide, 1.6 mM triethanolamine, pH 11.2
Voltage:	-18 kV
Temperature:	35 °C
Detection:	signal 350/50 nm, reference 235/10 nm
Preconditioning:	2 min flush with 0.1 N NaOH, 4.2 min flush with buffer, at 1 bar each

Anion analysis was performed using the Agilent Capillary Electrophoresis system equipped with diode array detection and computer control via the Agilent ChemStation. The chemical method is based on the Agilent Inorganic Anion kit. The pH of the buffer is raised to make sulfur species stable (for details see conditions next to figure). Migration times were stabilized by flushing the capillary with sodium hydroxide and buffer and replenishing buffer vials prior to each run. Available modification to the Agilent CE system provides for blanketing the replenishment system with helium to prevent oxidation of sulfide and sulfite anions. All standards (10,000 ppm sulfide, sulfate, Cl) were prepared in 0.1 N NaOH. Sample preparation consisted simply of diluting the sample 1:200 with water.

The assay was linear over the range 10 to 100 ppm with an $r^2 = 0.99997$. The detection limit in the Kraft liquors was approximately 1 ppm. Samples containing 20 g/L sulfide and 1 g/L of the other components could be routinely analyzed.

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