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Applications of capillary ion electrophoresis in the pulp and paper industry

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ABSTRACT

Alkaline (kraft) pulping of wood accounts for more than 60% of paper production. Anions critical to the performance of the kraft pulping process are presently determined by wet chemical methods and more recently by ion chromatography. Chemical recovery and liquor regeneration efficiencies are evaluated by monitoring these ions: Cl^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , SO_4^{2-} , S^{2-} , OH^- , and CO_3^{2-} , Na^+ and K^+ .

Capillary ion electrophoresis is a novel analytical technique that is optimized for the rapid monitoring of charged species. The technique is applied for the first time on kraft process streams using indirect UV detection at 254 nm and 214 nm to monitor the charged species. The results are used to evaluate important process variables such as sulfidity (white liquor), reduction efficiency (recovery furnace performance), and causticization efficiency (slaker performance).

This paper presents results obtained by off-line monitoring of ions found in the white, black and green liquors from kraft mills. The potential of capillary ion electrophoresis as a cost effective technique for rapid process processing of kraft pulping liquors is suggested.

INTRODUCTION

Chemical pulping of wood to obtain cellulose for the papermaking industry is a mature technology [1]. It consists of mixing inorganic chemicals with wood chips to separate lignin from the wood fibers. In the kraft pulping process lignin is removed by cooking wood chips in a aqueous solution of NaOH and Na_2S (white liquor). This white liquor contains smaller amounts of Na_2CO_3 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SO_3 . The spent liquor (black liquor) containing organic and inorganic anions is concentrated and burned in a Tomlinson recovery furnace to obtain a smelt of Na_2CO_3 and Na_2S . The molten sodium salts are dissolved to form the green liquor which is reacted with $\text{Ca}(\text{OH})_2$ to regenerate the white liquor. Fig. 1 illustrates the unit operations and chemical recovery cycle used in existing kraft mills.

In addition to monitoring the temperature/time profile of chip digestion, careful control of liquor

composition is critical to all phases of the operation. The composition of the liquors obtained from the combustion of the black liquor and regeneration of the white liquor will reveal whether targeted performance schedules have been met. To a great extent, it is the performance of the recovery operation which determines the quality of the product and the favorable economics of the kraft process.

Chemical components critical to the quality of pulping and make up of the liquors are the anions: hydroxide, sulfide, carbonate, sulfate, chloride, thiosulfate, sulfite. A significant portion of mill time is spent monitoring the concentrations of these anions to determine process performance. Analyses for these anions are performed off-line by various gravimetric and titrimetric procedures. Often on-line titrators and conductivity techniques are used to monitor the alkalinity and specific conductance respectively of the liquors.

Innovations in ion chromatography [2,3] and its

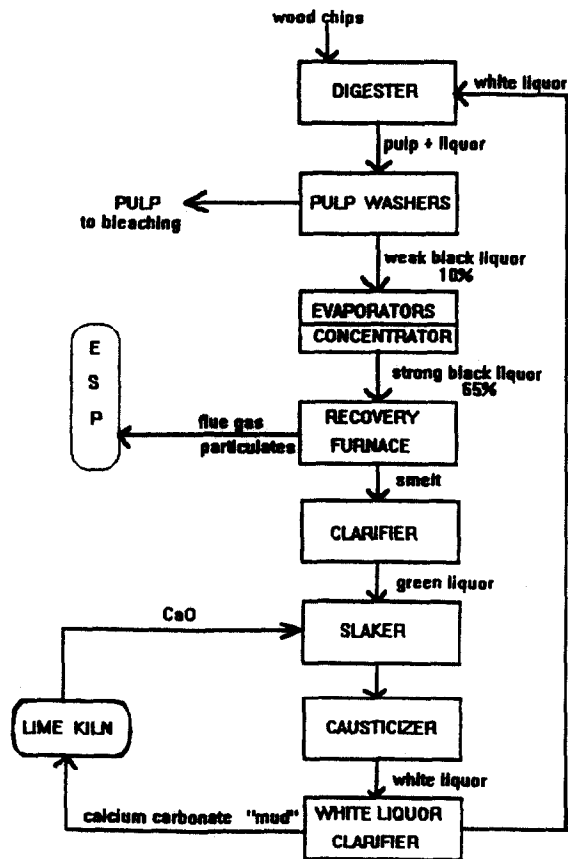


Fig. 1. Schematic illustrating the kraft process and the chemical recovery loop for the liquors. The cycle begins with the combustion of the black liquor in the recovery furnace. Recovered chemicals are converted to the green liquor. White liquor is regenerated in the causticizer and returned to the digester. ESP = Electrostatic precipitation.

application to process liquors [4-6] were significant in that analyses were simplified and ion specific. However, separation of all anions cannot be performed with one method. For example, the organic and inorganic anions present in the black liquor cannot be separated in one run. Furthermore, the determination of the cations in the liquors requires a different column and instrument stabilization before analysis.

Electrophoresis has developed into a powerful analytical tool for macromolecules [7,8]. In particular, capillary zone electrophoresis (CZE) with on-column detection is recognized as an important separation methodology for low molecular weight spe-

cies. State-of-the art reviews on CZE have been published [9,10]. The application of CZE to the analyses of small inorganic ions is exceptional because of selectivity, versatility, and the short time (minutes) required for development of a method [11].

Simplicity, speed, low operating costs, small sample size and ease of automation are some of the instrumental attributes to be considered for any analytical technology that has the potential for process monitoring. Capillary ion electrophoresis fulfils some of these criteria. Real time analyses for process monitoring and control at kraft plants should reduce operating costs, lower environmental emissions, and increase throughput.

This paper discusses results obtained by application of capillary ion electrophoresis to the analyses of kraft process liquors. It will be shown that CZE can monitor these complex process streams with little sample manipulation and with high speed compared with existing analytical methodologies.

EXPERIMENTAL

Instrumentation

The capillary electrophoresis system was a Quanta 4000 (Waters, Milford, MA, USA) equipped with a negative power supply for separation of anions. The applied voltage was 20 kV. For cations a positive power supply was used. Fused-silica capillaries of 60 cm \times 75 μ m I.D. and 60 cm length were obtained from Waters (AccuSep capillaries). The external capillary temperature was at 23°C. The detector window was formed by burning off a 10-mm section of the outer polyimide coating. Indirect UV detection was performed with a Hg lamp and a 254-nm optical filter. For determination of sulfide a zinc lamp with a 214 nm optical filter was used. Sample introduction into the capillary was by a 30-s hydrostatic injection from a height of 10 cm.

Electropherograms were recorded and processed with a Waters 860 Data Station and Waters SIM Interface. Data processing was performed with Waters Maxima 820 data station.

Reagents

Purified water (18 m Ω , Milli-Q; Millipore, Bedford, MA, USA) was used for all electrolytes, standards, and sample preparation. Containers for all

preparations were made of polyethylene. The anion standards were prepared by diluting 1000-ppm stock solutions containing a single anion.

The chromate electrolyte was prepared from a concentrate containing 100 mM Na_2CrO_4 (Malinckrodt analytical-reagent grade) and 0.069 mM H_2SO_4 (J. T. Baker, Ultrex grade). Electroosmotic flow (EOF) modifier for the reversal of the direction of EOF was obtained as a 20 mM concentrate from Waters (Nice-Pak OFM Anion-BT). The carrier electrolyte was prepared from 5 mM chromate and 0.5 mM electroosmotic flow modifier. The pH of the electrolyte was adjusted with 100 mM NaOH. Liquor samples were obtained from the respective process streams and were diluted 1:1000 with water and injected immediately. The $\text{Na}_2\text{S}_9 \cdot \text{H}_2\text{O}$ was obtained from Anachemia and used for making fresh sulfide solutions.

RESULTS AND DISCUSSION

Chemical recovery

As Fig. 1 illustrates wood chips are cooked in a digester with an aqueous solution of NaOH and Na_2S (white liquor) to remove the lignin. After bulk delignification the cellulose fibers are separated from the spent liquor (black liquor) and washed. The raw pulp is fed to the bleaching plant to complete the removal of lignin and to obtain a high quality pulp.

The chemical recovery cycle begins by concentrating the black liquor to about 70% solids. This concentrated black liquor is combusted in the recovery furnace to reclaim Na_2CO_3 , Na_2S and to generate process steam. The smelt ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{S}$) is dissolved to form the green liquor. This liquor is reacted with $\text{Ca}(\text{OH})_2$ to regenerate the white liquor ($\text{NaOH} + \text{Na}_2\text{S}$) which is returned to the digester. The precipitated lime mud (CaCO_3) is fed to the lime kiln to recover CaO which is used for the next cycle of liquor regeneration.

Kraft liquor anion analysis at 254 nm

An eleven-anion standard consisting of inorganic and organic ions is shown in Fig. 2. The concentration of each anion is 10 ppm. The pH of the standard sample was 10.6.

Fig. 3. shows the electrophoretic separation of a strong black liquor sample obtained in less than 8

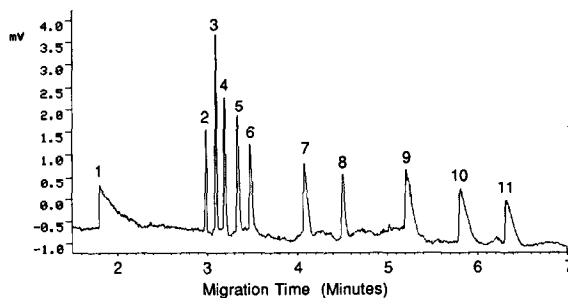


Fig. 2. Electropherogram of eleven-anion standard at 254 nm. Peaks: 1 = hydroxide; 2 = thiosulfate; 3 = chloride; 4 = sulfate; 5 = oxalate; 6 = sulfite; 7 = formate; 8 = carbonate; 9 = acetate; 10 = propionate; 11 = butyrate.

min. The inorganic anions are separated in less than 5 min. The sodium salts of the organic acids are the degradation products from the lignin and elute after the inorganics. Traditional wet chemical methods require several hours to perform the same analysis for the inorganic anions. Procedures for the analyses of liquors by suppressed ion chromatography (IC) have been developed [5,6,12]. The analysis by IC require two different methods in order to obtain similar results. CZE requires one method and therefore can deliver the analysis of this liquor in less time than IC.

Fig. 4 shows the electropherogram for a white liquor sample obtained by indirect UV detection. The presence of thiosulfate, sulfate and carbonate in the liquor are the "dead load" of the operation

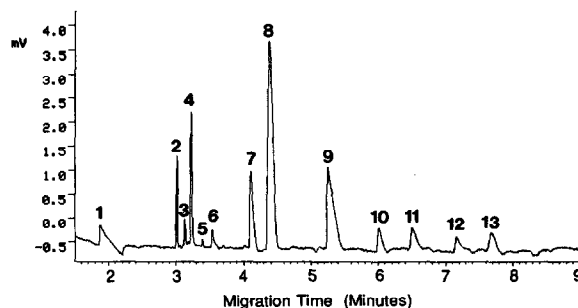


Fig. 3. Electropherogram of kraft strong black liquor. Conditions: Fused-silica 60 cm \times 75 μm capillary; voltage 20 kV (negative); 5 mM chromate electrolyte with Nice-Pak OFM Anion BT at pH 10.6; injection: hydrostatic for 30 s at 10 cm, indirect UV detection at 254 nm. The sample was diluted 1:1000 with water. Peaks: 1 = hydroxide; 2 = thiosulfate; 3 = chloride; 4 = sulfate; 5 = oxalate; 6 = sulfite; 7 = formate; 8 = carbonate; 9-13 = sodium salts of organic acids.

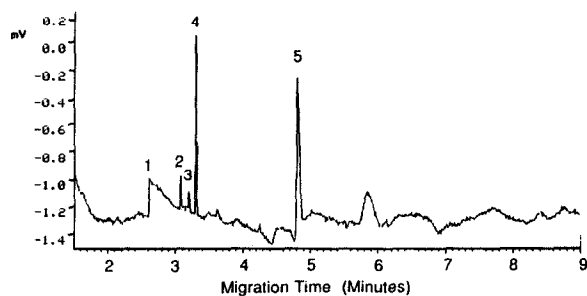


Fig. 4. Electropherogram showing the separation and indirect detection at 254 nm of a white liquor. The sample was diluted 1:10 000 with water; other conditions as in Fig. 2. Peaks: 1 = hydroxide; 2 = thiosulfate; 3 = chloride; 4 = sulfate; 5 = carbonate.

since these ions do not contribute to lignin removal. The amount of each ion correlates with the performance of the recovery furnace and slaker operations. A high thiosulfate and sulfate indicates poor reduction efficiency in the recovery furnace. A high carbonate content of the liquor following causticization operation indicates poor slaker performance.

Fig. 5 and 6 show electropherograms for samples from the digester at 45 and 75 min respectively. The increase of the organic acids (sodium salts) is evidence for lignin degradation. Analysis of this liquor can show the loss in sulfidity and alkalinity during the cooking of the wood chips.

Kraft liquor cation analysis at 214 nm

An electropherogram of the cations found in the black liquor is presented in Fig. 7. As expected sodium is the principal cation found in all liquors

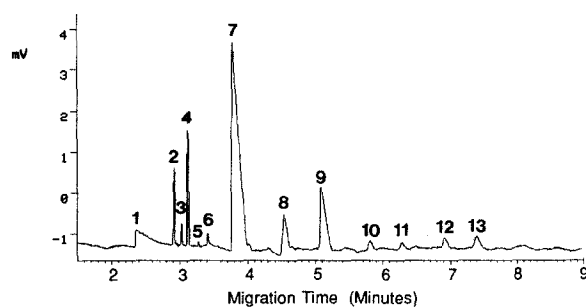


Fig. 5. Electropherogram of digester liquor after 45 min of pulping. Conditions as in Fig. 2: Peaks: 1 = hydroxide; 2 = thiosulfate; 3 = chloride; 4 = sulfate; 5 = oxalate; 6 = sulfite; 7 = formate; 8 = carbonate; 9–13 = sodium salts of organic acids.

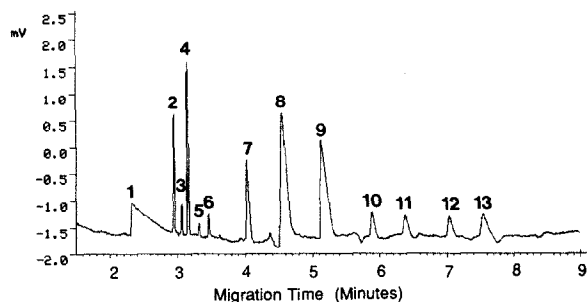


Fig. 6. Electropherogram of digester liquor after 75 min of pulping. Peaks as in Fig. 5.

(about 20%). Sodium is measured in order to assess where in the process there is significant soda loss. The potassium ion (less than 1%) is from the wood. Its accumulation in the liquor affect the combustion characteristics of the black-liquor fuel going to the recovery furnace.

Kraft liquor anion analysis at 214 nm

A spectrum comparing the absorbance of the chromate electrolyte with sodium sulfide at pH 11 is shown in Fig. 8. At 214 nm the hydrosulfide ion absorbs more strongly than the electrolyte at 214 nm. At 254 nm the absorptions are reversed with the result that the residual absorption of the hydrosulfide ion make it less sensitive to indirect photometric detection.

A six-anion standard is shown in Fig. 9. The hydrosulfide and thiosulfate ions are measured directly at this wavelength while the other ions are detected indirectly and with opposite polarity.

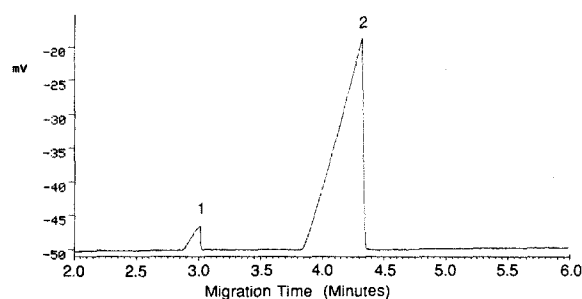


Fig. 7. Electropherogram for cations in black liquor. Carrier electrolyte 5 mM Waters UV Cat 1, 6.5 mM hydroxyisobutyric acid, pH 4.4, hydrostatic injection 30 at 10 cm, indirect UV detection at 214 nm. Peaks: 1 = potassium; 2 = sodium. Sample dilution was 1:1000 with water.

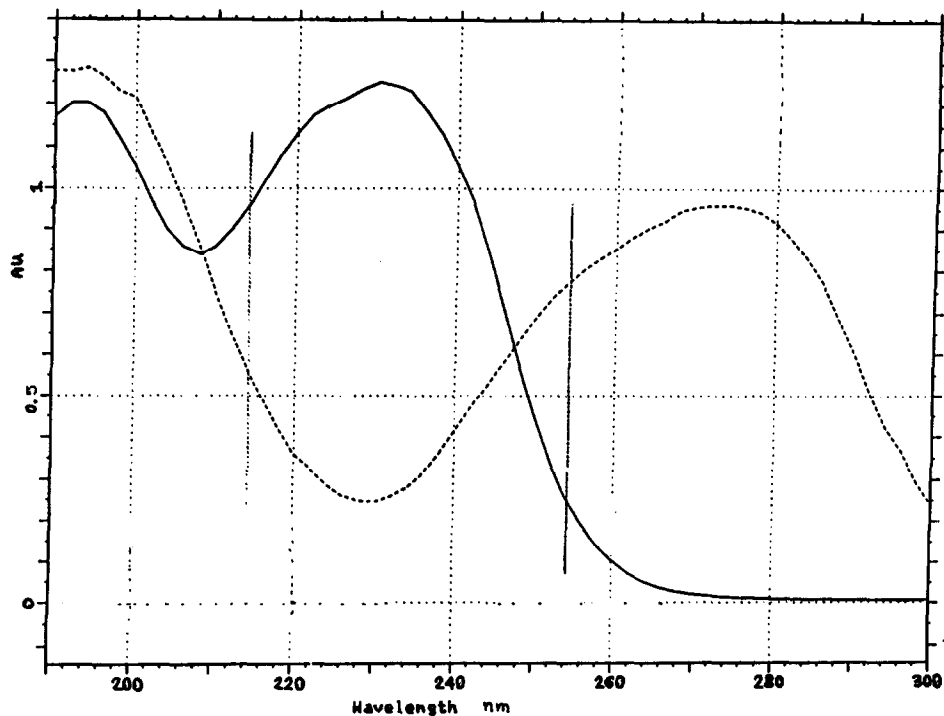


Fig. 8. Spectral overlay of chromate electrolyte (----) and sodium sulfide (—) at pH 11.

Analysis for carbonate, sulfide and sulfate ions is difficult to accomplish in one run by IC. These ions are critical for monitoring the performance of the recovery furnace and regeneration of the white liquor. Fig. 10 shows the electropherogram for a

green liquor sample. The significance of this analysis is that the reduction efficiency of the recovery furnace can be monitored. Information on the reduction efficiency allows adjustment to be made to the recovery furnace either via black liquor feed or

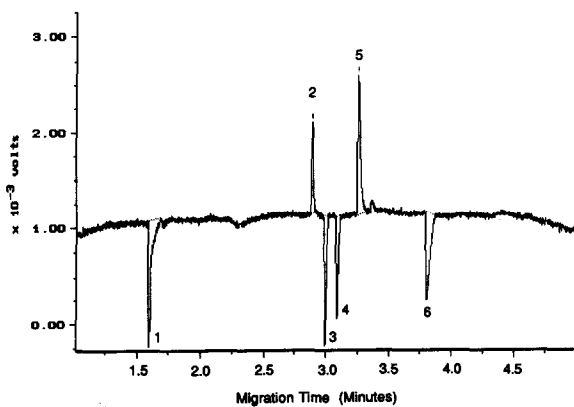


Fig. 9. Six-anion standard at 214 nm. Peaks: 1 = hydroxide; 2 = thiosulfate; 3 = chloride; 4 = sulfate; 5 = hydrosulfide; 6 = carbonate. Thiosulfate and hydrosulfide detected directly at this wavelength.

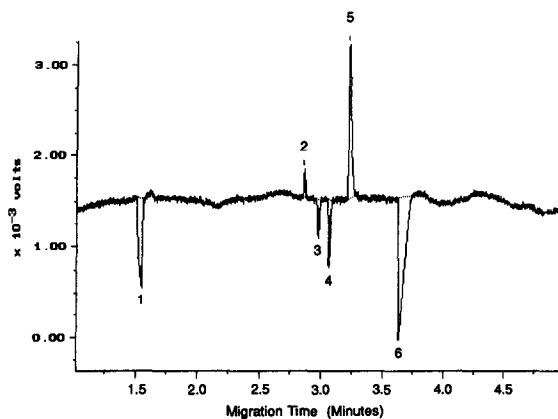


Fig. 10. Electropherogram of green liquor sample at 214 nm. The sample was diluted 1:10 000 with water; other conditions as in Fig. 9. Peaks: 1 = hydroxide; 2 = thiosulfate; 3 = chloride; 4 = sulfate; 5 = hydrosulfide; 6 = carbonate.

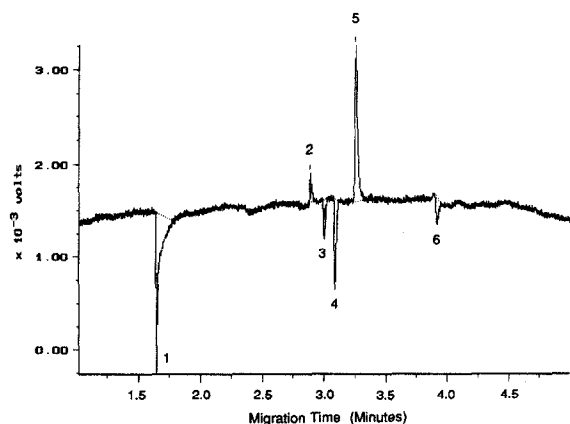


Fig. 11. Electropherogram of white liquor sample using 214 nm detection. Conditions as in Fig. 9. Peaks: 1 = hydroxide; 2 = thiosulfate; 3 = chloride; 4 = sulfate; 5 = hydrosulfide; 6 = carbonate.

air feed to the furnace. Thus, optimization and troubleshooting can be performed on the recovery system at a faster rate than could be performed by IC. Process problems can be addressed effectively and the operation run more evenly, resulting in lower operating costs.

Fig. 11 is from a white liquor sample with a pH for the diluted sample of 11.8. At this pH the principal species is the HS^- ion and therefore the peak in the corresponding electropherogram is identified as

TABLE I

REPEATABILITY OF MIGRATION TIMES FOR SAMPLE ANIONS AT pH 10.6 AND 11

Mean values of three analyses \pm relative standard deviation (R.S.D.). Conditions: 5 mM chromate electrolyte with 0.5 mM electroosmotic flow modifier. Liquor samples were diluted 1:1000 with water.

Anion	pH 10.6		pH 11	
	Migration time (min)	R.S.D. (%)	Migration time (min)	R.S.D. (%)
Hydroxide	2.7	4.5	1.7	6.9
Thiosulfate	3.0	2.8	2.9	2.0
Chloride	3.1	2.4	3.0	2.0
Sulfate	3.2	2.2	3.1	0.56
Carbonate	4.7	2.9	3.7	3.1

this ion [13]. Sulfide has been detected at 215 nm by IC [12].

Table I summarizes the repeatability of the migration time of the anions that were analyzed at pH 10.6 and 11. As expected the migration times decrease with increasing pH. The hydroxide ion has the largest deviation. This is probably due in part to its higher mobility compared to the chromate ion (198 vs. 85) making it (OH) more susceptible to local electric field variations. The peak shape asymmetry (tailing) is opposite to that predicted for an analyte with higher mobility than the electrolyte [14].

Mixing of the green liquor with Ca(OH)_2 converts Na_2CO_3 to NaOH and CaCO_3 . The recausticization efficiency can be calculated by monitoring the carbonate and hydroxide ions. Table II lists the important ions which make up the various liquors and their significance to the process. The causticization efficiency for this liquor was found to be 81.8% while the plant value determined by titration was 84.5%. For the sulfidity we obtained 33.7% and the plant value was 24.5%. The higher value obtained for the sulfidity is due to the greater uncertainty in

TABLE II

PROCESS SIGNIFICANCE OF ANIONS MONITORED AT KRAFT MILLS

The correlation of anions to the kraft process variables such as sulfidity, reduction and causticization efficiencies are given below. Chloride and oxalate are potential corrosion indicators.

Anions/stream	Black	White	Green	Process significance
Hydroxide		×	×	Causticization performance
Sulfide	×	×	×	Liquor quality
Carbonate		×	×	Slaker performance
Sulfate	×		×	Furnace performance
Thiosulfate	×		×	Oxidation
Sulfite	×		×	Oxidation
Chloride	×	×	×	Corrosion
Oxalate	×			Scaling

Process variables (chemicals in g/l):
 Reduction (%) = $100 \cdot \text{Na}_2\text{S} / (\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4)$
 Sulfidity (%) = $100 \cdot \text{Na}_2\text{S}^2 / (\text{Na}_2\text{S} + \text{NaOH})$
 Causticization (%) = $100 \cdot \text{NaOH} / (\text{NaOH} + \text{Na}_2\text{CO}_3)$

determination of the hydroxide ion by the present CZE methodology. Further work will address the quantitation of the hydroxide anion and its peak shape asymmetry.

CONCLUSIONS

Table II shows the ions that were monitored by CZE and their significance to the kraft pulping process. The advantages of this analytical technique are speed, simplicity, significant time savings, and minimal consumption of reagents for the analyses. Process diagnostics and troubleshooting can be implemented rapidly. Method development is faster than any currently available analytical technique and at a lower operating cost. All ions can be monitored conveniently at 214 nm.

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REFERENCES

- 1 J. R. G. Bryce, in J. P. Casey (Editor), *Pulp and Paper*. Wiley, New York, 1980, p. 377.
- 2 H. Small, T. S. Stevens and W. S. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- 3 D. T. Gjerde, G. Schmuckler and J. S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
- 4 G. O. Franklin, *Tappi*, 65 (1982) 107.
- 5 J. Krishnagopalan, M. Hill and A. L. Fricke, *Tappi*, 68 (1985) 108.
- 6 D. B. Easty and J. E. Johnson, *Tappi*, 70 (1987) 109.
- 7 J. W. Jorgenson, *Anal. Chem.*, 58 (1986) 743A.
- 8 F. Foret and P. Boček, *Electrophoresis*, 11 (1990) 661.
- 9 A. G. Ewing, R. A. Wallingford and T.M. Olefirowicz, *Anal. Chem.*, 61 (1989) 292A.
- 10 R. Wallingford and A. Ewing, *Adv. Chromatogr.*, 29 (1989) 1.
- 11 W. R. Jones and P. Jandik, *Am. Lab.*, 22 (1990) 51.
- 12 *Technical Association of the Pulp and Paper Industry*, Vol. 2, TAPPI Press, Atlanta, GA, 1991, Official Test Method T699 om-87.
- 13 J. N. Butler, *Ionic Equilibrium—A Mathematical Approach*, Addison-Wesley, Reading, 1964.
- 14 F. E. P. Mikkers, F. M. Everaerts and Th. P. E. M. Verheggen, *J. Chromatogr.*, 169 (1979) 1.