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Analysis of hydroxide, inorganic sulphur species and organic anions in kraft pulping liquors by capillary electrophoresis

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Abstract

A new method has been developed for the determination of hydroxide, sulphide, thiosulphate, sulphate, sulphite, chloride, oxalate and formate in kraft green, white and black liquors by capillary electrophoresis. The method provides baseline resolution of all analytes of interest using an electrolyte composed of 10 mM sodium chromate and 2 mM tetradecyltrimethylammonium hydroxide. Separations are conducted under constant current conditions at 25 °C and analytes are quantified by indirect UV-detection at 275 nm. A brief, post run wash of the capillary with 0.5 M NaOH and water gave improved inter- and intra-run repeatability of both migration times and peak areas. Sulphide and other oxysulphur species were relatively stable in white and green liquors diluted in helium-sparged water. However, sulphide present in black liquor samples diluted in the same solvent underwent rapid oxidation to form sulphite and thiosulphate, thereby precluding the measurement of all three anions. We discovered that quinone-type compounds present in black liquor catalyze the oxidation of sulphide and that the addition of reduced glutathione at a concentration of 1 mg/mL during black liquor dilution completely stabilized sulphide, sulphite and thiosulphate for at least one hour, thus allowing for quantitative analysis of the analytes. A mechanism is proposed to explain the action of both quinones and that of glutathione. Results obtained by the new method compared well with those obtained by ion chromatography, titrimetry, and from spike-recovery experiments.

Keywords: Kraft liquors; Sulphur compounds; Inorganic anions; Organic acids; Sulphides; Hydroxide; Glutathione

1. Introduction

Careful monitoring and control of the composition of white, green and black liquors is essential to ensure the production of high quality pulp and the economic viability of the kraft process. To meet this need, several titrimetric and gravimetric methods for determining hydroxide, carbonate, sulphide, sulphite, sulphate and thio sulphate in kraft liquors have been developed and used for more than 50 years [1–3]. More recently, several complexometric, potentiometric and/or conductometric methods have also been proposed [4–7]. These methods, however, vary in their scope and most are rather time consuming. Moreover, many are not suitable for the analysis of black liquors, nor do they allow for the analysis of other important species such as chloride and organic acids.

Over the last decade, ion chromatography (IC) has become a widely accepted technique for the determination of the major inorganic sulphur anions in kraft process liquors. While the IC methods allow for the quantitative analysis of a broader range of species, this is accomplished through the use of two or three different columns, eluent systems and detectors [8–11]. In addition, the columns are rather expensive and can become irreversibly fouled by organic substances present in complex samples such as kraft black liquor.

Flow injection analysis (FIA) methods have been developed for the determination of sulphur species in kraft mill liquors. While these approaches are simpler than IC methods, they are prone to interference when complex samples such as black liquor are analyzed and are limited in the number of analytes that can be determined. One FIA approach developed recently, utilizes UV, refractive index and conductivity detection to quantify hydroxide, sulphide and carbonate [12,13], while a second method employs colorimetry to determine sulphide only [14]. The main advantage of FIA over IC is that the use of expensive columns is eliminated.

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Recently, Fourier transform infrared (FT-IR) spectroscopy with attenuated total reflectance (ATR) and near infrared (NIR) transmittance spectroscopy has been adopted for determining sulphide, alkalinity and chloride in kraft liquors [15,16]. The IR methods use partial least-squares (PLS) multi-component calibration techniques to build spectral models for the analytes of interest. The methods have proven very useful for determining total alkalinity, sulphide and to a lesser extent chloride, in kraft green, white and black liquors. In addition, they do not require sample dilution or sample preparation prior to analysis and are thus amenable to on-line analysis. However, the IR-based approaches are quite limited in the number of analytes that can be determined and the types of samples that can be analyzed, since the composition of the samples must be known so that representative multi-component standards can be prepared and used in PLS calibration. In addition, the temperature at which the calibrations are performed must be closely controlled. Finally, the IR-based methods suffer from poor sensitivity.

Capillary electrophoresis (CE) is a relatively new technique with the potential to overcome several limitations found in the current titrimetric and instrumental approaches used for ion analysis. The attractive features of CE include: the ability to determine anions, cations and neutral species using the various modes of separation, short analysis times, high efficiency separations, universal modes of detection (i.e., indirect photometric), the ability to analyze complex samples with little sample preparation, and the ability to use relatively inexpensive capillary columns for most separations [17–22].

Work done by Jones [23,24] and Jandik and Bonn [25] has demonstrated that high-efficiency, high-speed separation of several anions is possible using a chromate electrolyte containing an electro-osmotic flow (EOF) modifier with indirect UV detection. Following this work, Salomon and Romano demonstrated the feasibility of using a chromate/surfactant-based electrolyte system for separating anions in kraft mill liquors by CE [26]. Although their approach utilized and showed the potential of CE to separate key anions in kraft process liquors, the authors did not demonstrate that it was suitable for quantitative analysis. Subsequently, publications by other workers have appeared [27,28]. The authors again used a chromate-based electrolyte, which included polybrene (hexadimethrine bromide, HDB) to reverse the EOF and acetonitrile to manipulate the selectivity of the separation. While reasonably good resolution was obtained for most anions, poor resolution of sulphate from sulphide and formate from carbonate were obtained. Moreover, the authors did not demonstrate that their approach was suitable for quantitative analysis, and in fact, they noted that sulphide was very unstable in dilute black liquor samples.

In the current work, we describe a new CE method suitable for simultaneously separating and quantifying hydroxide, sulphide, sulphate, sulphite, thiosulphate, oxalate, formate, chloride and carbonate in kraft green, white and black liquors. We also report on the development of a simple and effective means of stabilizing sulphide in diluted black liquors and discuss the factors responsible for the degradation of sulphide in black liquors.

2. Experimental

2.1. Chemicals

Analytical grade sodium chromate tetrahydrate, tetradecyltrimethylammonium bromide (TTAB), sodium sulphide nonahydrate, sodium hydroxide, sodium sulphite, sodium sulphate, sodium thiosulphate, sodium chloride, sodium oxalate, sodium formate, sodium carbonate, barium chloride, sodium hydroxide, hydrochloric acid, mercuric chloride, glutathione (GSH, reduced form; GSSG, oxidized form), 1,4-benzoquinone (BQ), 2-hydroxymethyl-6-methoxy-1,4-benzoquinone (HMBQ), 2-hydroxy-1,4-naphthoquinone (HNQ), anthroquinone-2-carboxylic acid (AQCA), anthraquinone-1,5-disulphonic acid (AQDSA) and isopropanol were analytical or ACS reagent grade from Aldrich (Milwaukee, WI, USA). Water used throughout this work was from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2. Apparatus

2.2.1. CE instrumentation

CE analyses were performed with the aid of two different instruments. Instrument “A” was a Crystal 310 CE equipped with a 48-position autosampler and a Pye Unicam model 4225 UV/Vis detector, both from Thermo Bioanalysis (Franklin, MA, USA). Instrument control and data acquisition were conducted using DAx version 6 software from Prince Technologies (The Netherlands). The detector wavelength was set to 275 nm, the data acquisition rate was set to 20 Hz and the polarity of the detector signal was reversed so as to obtain positive peaks. Bulk fused-silica capillary tubing (75 μm i.d. × 363 μm o.d.) was obtained from Polymicro Technologies (Phoenix, AZ, USA). Individual capillaries with a total length (L_t) of 85 cm and effective length to detector (L_d) of 70 cm were cut from the bulk tubing with the aid of a ceramic knife. A detection window (ca. 5 mm wide) was created by burning off the polyimide coating with butane lighter. The window was then cleaned with a lens tissue wetted with acetone. All samples were injected with a pressure of 20 mbar for 15 s (300 mbar s).

Instrument “B” was a Hewlett Packard 3^{D}CE equipped with a diode array detector from Agilent Technologies (Pleasanton, CA, USA). Instrument control and data acquisition was done with HP ChemStation software, version A.08.03. To obtain positive peaks, the detection wavelength was set to 525 nm (BW 150 nm) and the reference wavelength was set to 275 nm (BW 10 nm). The data acquisition

rate was set to 10 Hz. Capillaries with 75 μm i.d. × 365 μm o.d. and L_t of 80.5 cm (L_d = 72 cm) were obtained from Agilent Technologies. All separations were performed under constant current conditions (−25 μA), at 25 °C, with a negative polarity applied to the inlet end of the capillary. All samples were injected with a pressure of 20 mbar for 15 s (300 mbar s).

2.3. Ion chromatography instrumentation

A Dionex model 4000i ion chromatography equipped with a quaternary gradient pump module (GPM), a conductivity detector (CDM-3), and an anion self-regenerating suppressor (ASRS) (Sunnyvale, CA, USA) was used for all ion chromatography studies. Chloride, sulphite, sulphate, thiosulphate, carbonate, oxalate and formate were determined using columns, eluents and other conditions outlined in published methods [8–10].

2.3.1. Titration instrumentation

All titrations were performed with a Metrohm model 682 titrator (Brinkmann Instruments (Canada) Ltd.) equipped with an auto burette, a glass pH probe Metrohm, a Ag/AgCl double junction reference electrode and a Ag/S ion selective electrode (ISE), both from Thermo Electron Corp. (Beverly, MA, USA). Titration of hydroxide and sulphide in kraft liquors was performed according to established methods [1,2,4,6]. Standard solutions of sodium sulphide and sodium hydroxide were prepared fresh daily in He-sparged water and titrated in duplicate, at least twice daily to ensure proper function of the probes and titration apparatus.

2.4. Electrolyte preparation

The background electrolyte used for CE analyses was comprised of sodium chromate tetrahydrate and tetradecyltrimethylammonium hydroxide (TTAOH). Running electrolyte solution was prepared daily by diluting stock 100 mM $Na_2CrO_4{\cdot}4H_2O$ and 20 mM TTAOH solutions with He-sparged Milli-Q water. Prior to use, the electrolyte was sonicated for 5 min and then filtered through a 25 mm × 0.5 μm PTFE Millex-LCR syringe filter (Millipore, Bedford, MA, USA). In the case of instrument A, filtered electrolyte was delivered to 4 mL glass autosampler vials (capillary inlet) and into a ca. 35 mL capillary outlet glass vial. The inlet side electrolyte was replaced every eight runs. In the case of instrument B, 0.6 mL filtered electrolyte was placed in 1 mL polypropylene vials from Agilent Technologies. The inlet side electrolyte was replaced after each run, and the outlet side electrolyte was replaced after ten runs. Stock TTAOH solution was prepared from TTAB in the following manner: Approximately 125 mL of 20 mM TTAB aqueous solution was allowed to flow under gravity through a 60 mL polypropylene syringe (BDH) containing 40 mL of washed Dowex-1 resin (Nuclear grade, OH form, 100 mesh) from Sigma (St. Louis, MO, USA). The last 100 mL of eluate was collected and stored in a 125 mL Nalgene polypropylene bottle [Fisher Scientific (Canada)] at 4 °C. Prior to use, Dowex-1 resin was washed with 50 mL of 1 M NaOH and at least 150 mL of Milli-Q water to remove excess NaOH.

2.5. Capillary cleaning protocol

At the beginning of each day, the capillary column was conditioned with 0.5 M NaOH and water for 10 and 5 min, respectively. Prior to each analysis, the capillary was rinsed with electrolyte for 3 min. After each analysis, the capillary was washed with 0.5 M NaOH and twice with water (using separate vials) for 3, 2 and 1 min, respectively. All column conditioning steps were performed at a pressure of 950 mbar. The use of separate water rinse vials ensures that NaOH is not carried over into the inlet electrolyte vial. The capillary was left filled with water between analyses and when not in use. All washing and rinsing steps were pre-programmed and carried out with the autosampler.

2.6. Standards and solutions

Standard sulphide solution (1000 mg/L as S^{2-}) was prepared daily according to the following procedure to minimize the oxidation of sulphide during the preparation and storage of standards. Several crystals of $Na_2S{\cdot}9H_2O$ were rinsed with small aliquots of water to remove oxysulphur species such as thiosulphate, which are present on the surface of the crystals and immediately dried by gently rolling the crystals between a lens tissue. The washed crystals were then transferred directly into a tarred volumetric flask and He-sparged water was added to the mark. The flask and its contents were then sonicated for 10 min or until the sulphide crystals were completely dissolved. After dissolution was complete, the flask was inverted two or three times, stored at 25 °C in the dark and was not mixed again thereafter. Both stock sulphide solutions and dilute standards were prepared fresh daily. All dilutions were done in He-sparged water unless specified otherwise.

Stock sulphite solution (1000 mg/L as SO_3^{2-}) was prepared daily. In order to minimize the oxidation of sulphite, the following procedure should be followed. An accurately known mass of sodium sulphite is placed in a small polypropylene weighing boat and the solid is transferred to a 100 mL volumetric flask containing 90 mL of 10% (v/v) isopropanol in He-sparged water, which had been sonicated for at least 5 min. Small portions of 10% isopropanol/water were used to rinse the weighing boat and for final dilution to volume. The flask and its contents were then sonicated for 10 min or until the sulphite crystals were completely dissolved. Once dissolution was complete, the flask was inverted twice and was not mixed again thereafter. The stock solution was stored at 25 °C.

Standard 1000 mg/L solutions of thiosulphate, sulphate, chloride, oxalate and formate were prepared by dissolving

the sodium salts of each reagent in water. The solutions were stable for at least 6 months when stored in the dark at room temperature. Dilute mixed standards containing a range of concentration of the various ions were prepared daily by combining aliquots of the various stock solutions and standard 1 M NaOH followed by dilution to volume with He-sparged water. The concentration of NaOH in each standard was kept constant at 10 mM. It was found that all anions were stable in the mixed standards over the course of a day. Standard solutions of NaOH were prepared by diluting standard 1N NaOH in He-sparged water. Stock GSH solution (10 mg/mL) was prepared daily by delivering 500 mg of GSH and 2.5 mL of 2 M NaOH to a 50 mL PMP volumetric flask and then diluting to volume with He-sparged water. GSH solutions were stored at 4 °C in polypropylene bottles and prepared fresh daily. All solutions and samples were prepared and stored in polymethylpentene (PMP) flasks (Fisher Scientific).

Stock solutions containing 1000 mg/L of each of the model quinones (see Chemicals) were prepared by dilution of each compound in He-sparged water. For quinone/sulphide stability studies, suitable aliquots of each of the quinones and sulphide stock solutions were combined in a volumetric flask and diluted to volume to give a final concentration of 10 mg/L of each analyte. Once prepared, the quinone/sulphide solutions were analyzed immediately and at regular intervals thereafter to determine the concentration of sulphide and oxysulphur anions that may have formed.

2.7. Preparation of samples

Samples of green (GL), white (WL) and black (BL) liquors were obtained from Canadian kraft mills and stored at 4 °C. All samples were kept refrigerated and were warmed to room temperature, mixed, diluted in He-sparged water, filtered through a 25 mm × 0.5 μm PTFE Millex-LCR syringe filters (Millipore) prior to injection into the CE. In the case of black liquors, the following dilution procedure was used to minimize the oxidation of sulphide: to a 100 mL volumetric flask was added 80 mL of He-sparged water, 10 mL of stock GSH solution (10 mg/mL GSH) and 0.40–0.50 mL of filtered black liquor. The contents of the flask were then quickly diluted to volume with He-sparged water, briefly mixed and analyzed within 1 min.

3. Results and discussion

3.1. Analysis of kraft liquors by CE

Attempts to use the method by Salomon and Romano for the analysis of anions in kraft liquors [26], revealed several problems which seriously limited the usefulness of the approach, including: (1) an inappropriate wavelength for determining sulphide, (2) an unsuitable electrolyte composition for resolving oxalate and sulphide and (3) large variations in migration times between standards and samples as well as poor migration time reproducibility. It was necessary, therefore, to resolve these problems before the technique could be of practical value for routine analysis of pulp and paper process liquors. As described in the following sections, we have developed several strategies to overcome these problems.

3.1.1. Detection wavelength and electrolyte considerations

Ideally in indirect photometric detection, a wavelength at or close to the absorption maximum of the background electrolyte co-ion is normally chosen. However, in some instances, this may not be possible because the analyte(s) of interest may have a significant absorbance at the wavelength maxima of the co-ion. In the current situation, both sulphide and chromate absorb quite strongly at the two wavelengths used by Salomon and Romano (214 and 254 nm) and therefore, both wavelengths are less than ideal for quantifying sulphide. However, this problem can be resolved quite simply by exploiting the fact that chromate has absorption maxima near 275 and 375 nm, both of which are in regions where neither sulphide nor the other analytes of interest absorb. Consequently, indirect-detection could be done at 275 and/or 375 nm. In principle, detection limits at 375 nm should be better than those obtained at 275 nm because of the higher absorptivity of chromate at the former wavelength. However, we found that the signal-to-noise (S/N) ratio at 275 nm was significantly better than that at 375 nm and therefore chose to use the former wavelength in our work. When we used the electrolyte system described by Salomon and Romano and detection at 275 nm, we found that most anions were well resolved, with the exception of sulphide and oxalate, which were found to co-migrate. We also found considerable variations in the migration times of the analytes between runs.

In an effort to overcome the co-migration problem and improve the repeatability of the migration times, we set out to optimize the electrolyte composition so as to achieve complete resolution of all analytes in a single run. Several electrolytes containing chromate and TTAOH concentrations in the range of 4–12 mM and 0.25-2.0 mM, respectively were prepared and used to analyze standard mixtures of the anions of interest. In addition, all separations were conducted under constant current (−25 μA) rather than constant voltage conditions in an effort to improve migration time repeatability (for the reasons mentioned in the section below). From this study we found that an electrolyte composed of 10 mM chromate and 2 mM TTAOH yielded baseline resolution of all analytes of interest for both standard mixtures and samples of kraft liquors, as illustrated in Figs. 1 and 2. In addition, we found that migration times were much more reproducible and only small shifts in the migration times of analytes in standards and in kraft liquors were noticed, which was not the case when constant voltage was used for the separations. Under constant voltage conditions, migration

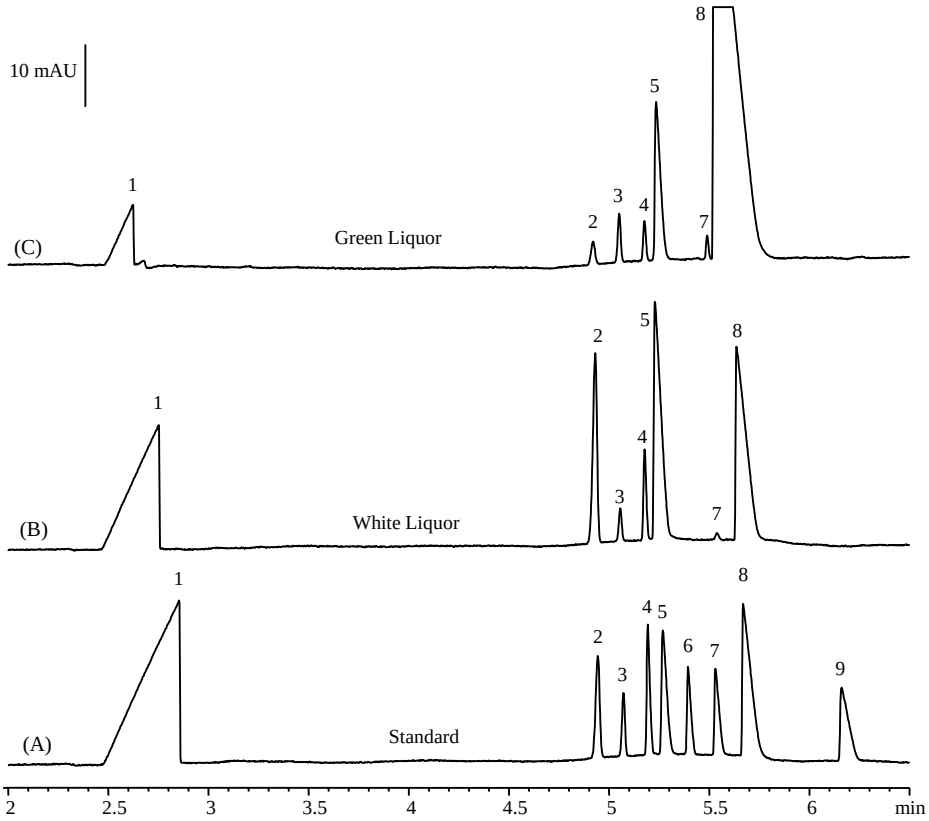

Fig. 1. CE separation of anions in a standard mixture (A), in white liquor diluted 1:500 (B) and in green liquor diluted 1:500 (C). Standard mixture contained 10 mM NaOH and 10 mg/L of each anion. The standard mixture and samples were prepared in He-sparged water. Peak identities: hydroxide (1), chloride (2), thiosulphate (3), sulphate (4), sulphide (5), oxalate (6), sulphite (7), carbonate (8) and formate (9). CE separation conditions using instrument B: capillary column, 80.5 cm (L_t) × 75 μm i.d.; pressure injection, 20 mbar for 15 s.; electrolyte, 10 mM sodium chromate tetrahydrate containing 2 mM TTAOH; temperature and applied current, 25 °C and −25 μA, respectively; detector settings, signal set to 525 nm (bandwidth 150 nm), reference signal set to 275 nm (bandwidth 10 nm). See text and Section 2 for further details.

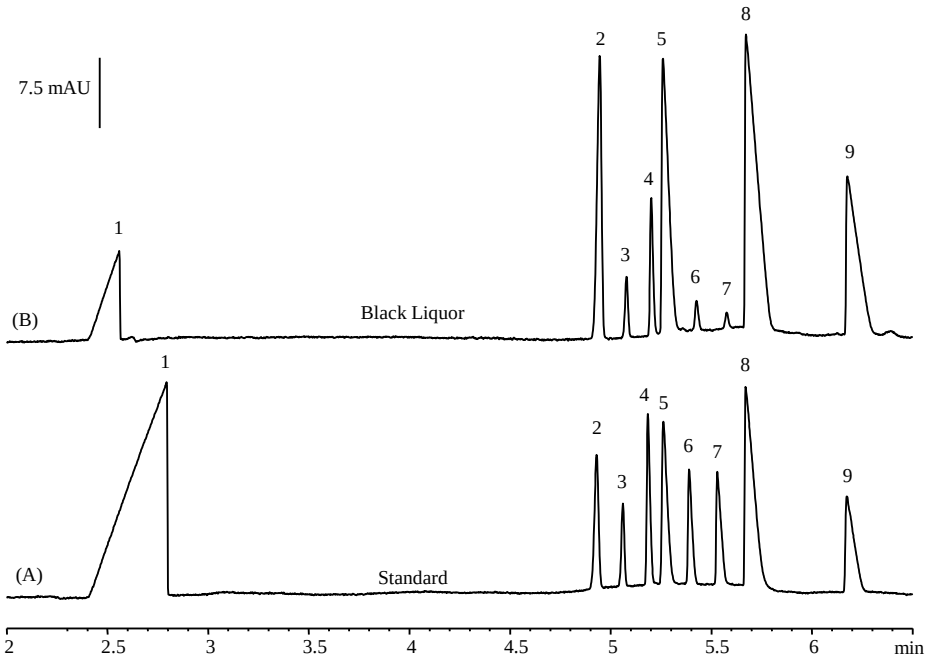

Fig. 2. CE separation of anions in a standard mixture (A) and in black liquor diluted 1:200 in He-sparged water containing 1 mg/mL GSH (B). Peak identities and CE separation conditions as indicated in Fig. 1. See text and Section 2 for further details.

time shifts were significant between standard mixtures and samples.

3.1.2. Factors controlling migration time repeatability

The pH of an electrolyte system used in CE separations influences the electrophoretic mobility of the analytes and the magnitude of the EOF, which in turn affects the selectivity of the separation and can influence the reproducibility of the migration time if not controlled within fairly narrow limits. An inherent characteristic of the chromate-based electrolyte system is its low buffering capacity and relatively low ionic strength (in most CE applications). Because of the low buffering capacity, this type of electrolyte is very susceptible to changes in pH, which occur as a result of electrolysis brought about by the high voltages used in the separations. Electrolysis leads to an increase in the pH at the cathode (capillary inlet), where OH^- is formed and a decrease in pH at the anode, where H^+ ions are formed [29]. Consequently, it is imperative that the inlet electrolyte be replaced frequently. It is known that the velocity of the EOF (v_{EOF}) is linearly related to the field strength (E) and to the current (I) flowing through the capillary [30]. Because inorganic anion separations are usually conducted under co-electro-osmotic flow conditions (EOF and anion migration are in the same direction), it follows that an increase in either voltage or current will produce an increase in EOF, which results in a decrease in analyte migration time. Performing separations under constant current conditions, would be expected to yield more reproducible migration times than those obtained under constant voltage conditions [31,32], especially if the electrolyte used has low buffering capacity and the conductivity of the samples under investigation vary greatly or are quite different from that of the standard anion solutions used for calibration purposes, as is the case for kraft liquors.

Another potential contributor to poor migration time reproducibility may arise from deposition or adsorption of dissolved substances such as lignin, polysaccharides and lipophilic extractives present in black liquor onto the inner surface of the capillary column. The adsorbed substances can alter the zeta potential at the inner surface of the capillary and thus affect the EOF. If the substances are not removed after each run, analyte migration times will vary considerably from run-to-run. To address the issue of capillary column contamination, which is particularly prone to occur when analyzing black liquors, a column cleaning procedure utilizing 0.5 M NaOH and water rinses at the end of each run was implemented. This concentration of NaOH is very effective in removing adsorbed organic material from the inner surface of the capillary column after each run.

CE analysis of standard mixtures of the anions of interest gave linear relationships between peak area and concentration in the range of 0.5–50 mg/L for each analyte (1–50 mM for NaOH), with correlation coefficients of 0.999 or better. Replicate analysis of the standards gave R.S.D.s of 0.2 and 1–3% for migration times and peak areas, respectively for the anions of interest.

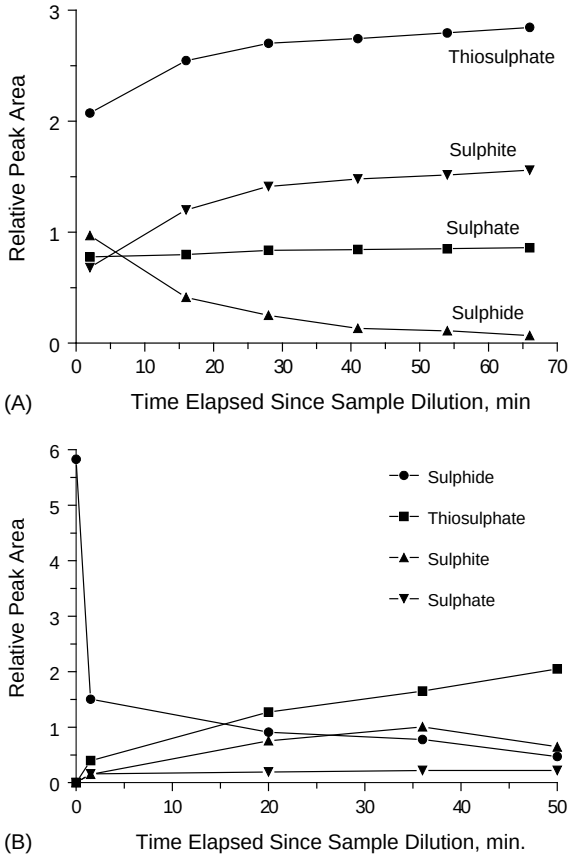

Fig. 3. Variation in the peak area of sulphide, thiosulphate, sulphite and sulphate as determined by CE, in black liquor diluted 1:200 in Milli Q-water (unsparged), no GSH present (A) and in the presence of aqueous 1,4-benzoquinone, no GSH present (B). See text and Section 2 for further details.

Replicate analysis of samples of WL, GL and BL were performed to assess the repeatability of the migration times and peak areas for the various kraft liquors. This was done by diluting the samples (200–500 times) in He-sparged water and repeatedly injecting the solution over the course of an hour. Excellent migration time repeatability with R.S.D.s in the 0.1–0.2% range was obtained for all analytes, in agreement with our findings with standard anion solutions. With the exception of sulphide, thiosulphate and sulphite in black liquor samples, peak area repeatability was also very good (R.S.D.s in the 1–3% range). In contrast, the R.S.D.s for the peak areas of sulphide, thiosulphate and sulphite in black liquors were 32, 9 and 13%, respectively. Upon closer examination of the data, we found that the peak area for sulphide in a diluted sample of black liquor decreased steadily over time, while those for thiosulphate and sulphite increased, as illustrated in Fig. 3A. This data suggested that sulphide was being oxidized very quickly in black liquor for some unknown reason.

3.1.3. Role of quinones in sulphide oxidation

Based on the findings described above, we postulated that lignin present in black liquor was somehow accelerating

the oxidation of sulphide. Kraft lignin is a complex and not completely characterized polymeric material, which is known to contain quinone-type structures that are thought to play a key role in catalyzing the oxidation of sulphide. To test this hypothesis, we studied the stability of aqueous sulphide solutions containing several different quinones (see Section 2) using our CE method. The study showed that among the model quinones investigated; only HMBQ and BQ were capable of catalyzing the oxidation of sulphide. HMBQ reacted with sulphide to form thiosulphate exclusively, while BQ reacted with sulphide to yield both thiosulphate and sulphite, which was strikingly similar to the oxidation products formed in diluted black liquors, as illustrated in Fig. 3B. Based on these findings, we postulated that BQ may be involved in a redox couple between oxygen and sulphide, whereupon BQ cycles between its oxidized and reduced forms, and in the process transfers electrons from sulphide to oxygen, resulting in the oxidation of sulphide to thiosulphate and sulphite and the formation reactive oxygen species such as superoxide radical anion and perhaps hydrogen peroxide. We also hypothesized that it might be possible to prevent quinone catalyzed oxidation of sulphide by adding a free radical scavenger during the sample dilution step. The radical scavenger should react rapidly with free radicals such as semiquinone radical anion and superoxide radical anion, and therefore break the redox couple and thereby halt or minimize the catalytic effect of quinones in the oxidation of sulphide. To be useful in CE analysis, the radical scavenger must not perturb the CE separation or co-migrate with any of the analytes of interest.

3.1.4. Development of a strategy for stabilizing sulphide using GSH

One of the major candidates that we considered for stabilizing sulphide was the reduced form of glutathione (GSH), which functions very effectively as a free radical scavenger in the cells of living organisms [33]. We tested our hypothesis by conducting several experiments with aqueous sulphide solutions containing BQ, and in the presence and absence of various concentrations of GSH. Our study revealed that sulphide was completely stabile for up to 1 h when GSH was present at a concentration of 1 mg/mL. We found a similar effect when black liquor was diluted in He-sparged water containing 1 mg/mL of GSH, as illustrated in Fig. 4A. In addition, thiosulphate, sulphite and sulphate were also stable over the same period of time in the presence of GSH, as shown in Fig. 4B–D, respectively. As the figures illustrate, the greatest stability was always obtained when GSH and He-sparged water were used together. Dilution of black liquor in water containing less than 1 mg/mL GSH were not as effective at stabilizing sulphide.

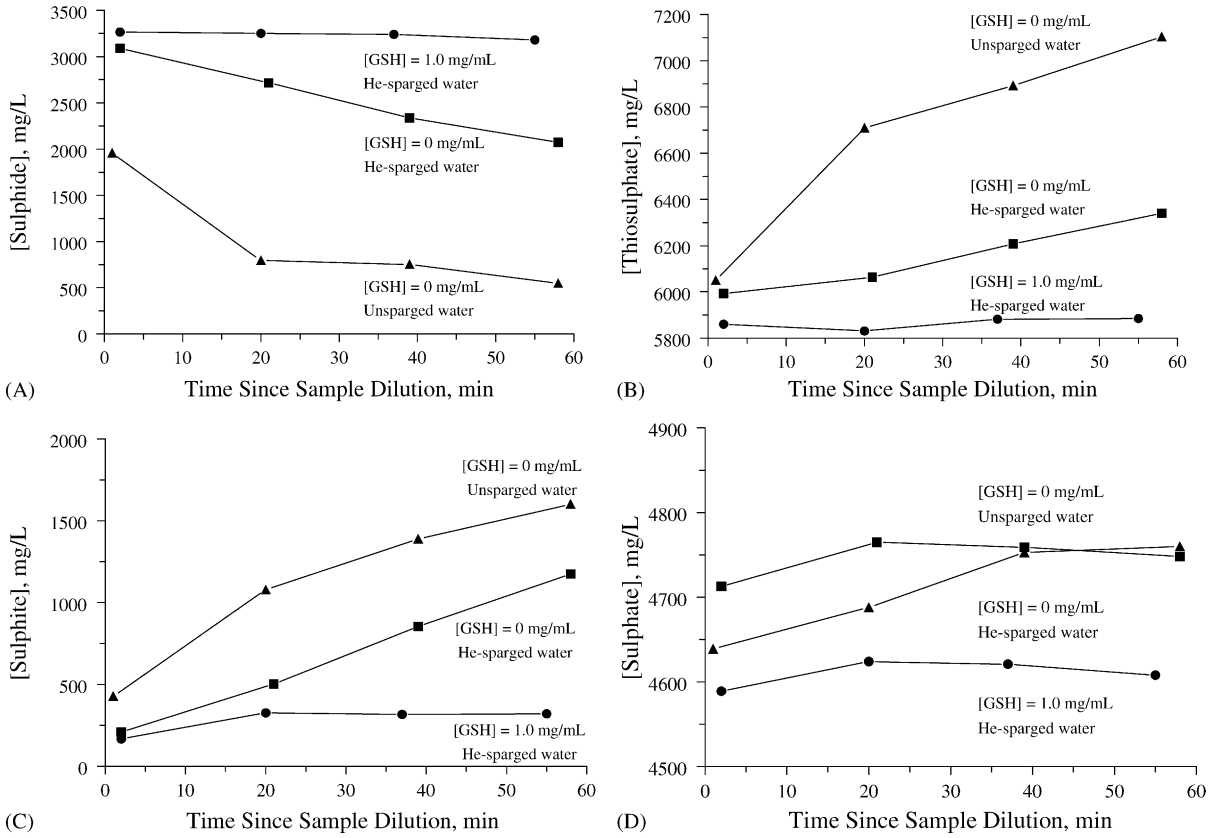

Fig. 4. Variation in the concentration of sulphide, thiosulphate, sulphite and sulphate (A–D, respectively) in black liquor diluted 1:200 in Milli Q-water (unsparged and He-sparged), with and without GSH present. See text and Section 2 for further details.

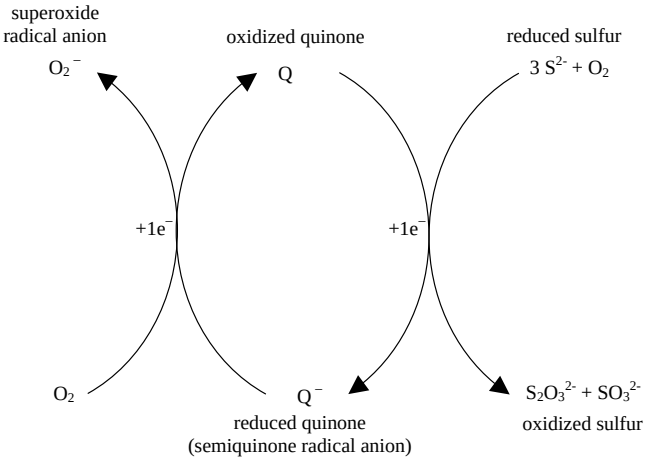

Fig. 5. Proposed mechanism to explain the oxidation of sulphide in the presence of quinones.

A possible mechanism by which sulphide oxidation occurs in the presence of quinones and by which it is inhibited by GSH is shown in Fig. 5. In this scheme, the redox cycle begins when oxidized quinone accepts an electron from sulphide, which causes the oxidation sate of sulphur to decrease, thereby promoting the reaction between sulphide and traces of dissolved oxygen present in the dilution water, and at the same time resulting in the formation of reduced quinone (semiquinone radical anion). Reduced quinone then transfers an electron to traces of oxygen present in the dilution water, resulting in the formation of highly reactive oxygen species such as superoxide radical anion and perhaps hydrogen peroxide as well. The newly formed oxidized quinone is now capable of reacting again with sulphide as described above, and to ultimately converting all of the sulphide to thiosulphate and sulphite. The redox cycle will continue as long as traces of oxygen and sulphide are present to drive it. When GSH is introduced into this system, we suspect that it reacts with the two major radical anions as they are produced in the redox cycle, resulting in the formation of $GS^{\bullet -}$, which, then reacts with each other to form oxidized glutathione ($2GS^{\bullet -} \rightarrow GSSG$). In essence, we believe that GSH scavenges electrons from superoxide and semiquinone radical anions, and thus halts the redox cycle between quinones and sulphide. Consequently, quinones cannot cycle between their oxidized and reduced forms, and therefore cannot accept electrons from sulphide. However, once all or a significant fraction of the GSH becomes oxidized, the quinone catalyzed oxidation of sulphide should resume and this is why sulphide is not permanently stabilized by GSH in the presence of quinones. Another important finding from our study was that neither GSH nor GSSG migrates in the time frame in which the anions of interest migrate. In fact, we found that GSH has a lower net mobility than formate, and GSSG has a migration time that is longer than GSH.

Table 1
Analysis of sulphur species, chloride, oxalate and formate in black liquor by CE, IC and titrimetry

Anion	Anion concentration (mg/L)		
	CE	IC	Titrimetry
Thiosulphate	5700	5900	–
Sulphate	1500	1500	–
Sulphide	3300	–	3400
Sulphite	420	400	–
Chloride	130	140	–
Oxalate	460	460	–
Formate	6000	5700	–

IC conditions as described in refs. [8–10]. Titrimetric analysis of sulphide was conducted using an Ag/AgS ISE, according to the method of Papp [4]. See text and Section 2 for other conditions.

3.1.5. Analysis of anions by CE and classical methods

The suitability of the new CE method for quantitative analysis was assessed by comparing results obtained from the CE analyses of kraft liquors with those obtained by IC, classical titrimetric methods and from spiking experiments.

As indicated in Table 1, CE results obtained for the various anions in black liquor were in good agreement with those obtained by IC and potentiometry. CE analysis of white and green liquors is significantly less complicated than it is for black liquors because the former samples are free from organic compounds such as quinones, and from organic compounds such as oxalate, which migrates at nearly the same velocity as sulphide and sulphite. As indicated in Table 2, sulphide results obtained by CE were within 1–2% of those obtained by titrimetric methods [1,2,4]. Analysis of oxysulphur species and chloride by CE and IC were also in good agreement as shown in Table 3. The largest discrepancies between the methods were found with sulphite (up to 15% for GL-E), and to a lesser extent chloride. The large differences in the sulphite results may be caused by the degradation of low levels of polysulphide (S_nS^{2-}) [34,35] present in this particular white liquor, during sample dilution, to form sulphite [8]. One other difficulty with the analysis of sulphite in this type of sample is the low level that is present after dilution. For example, liquor diluted 1:500 contains a sulphite concentration of about 0.5 mg/L, which is near the detection limit of the CE method. Samples of green and white liquor

Table 2
Analysis of sulphide in white and green liquors by CE and titrimetry

Liquor sample	Sulphide (g/L)			Ratio of CE to titrimetry	
	CE	Titrimery (ABC)	Titrimetry (ISE)	CE/ABC	CE/ISE
WL-D	9.6	9.8	9.8	0.98	1.00
WL-E	11.0	11.2	11.3	0.98	0.99
GL-E	11.9	11.7	11.4	1.02	1.04
GL-F	15.7	15.8	15.8	0.99	1.00
GL-G	17.4	17.6	17.7	0.99	0.98

See text and Section 2 for other conditions. Titrimetric analysis of sulphide was performed according to [1,4]. White and green liquors are designated as WL and GL, respectively.

Table 3
Analysis of oxysulphur species and chloride in white and green liquor by CE and IC

Anion	Anion concentration (mg/L)					
	WL-D		WL-E		GL-E	
	CE	IC	CE	IC	CE	IC
Thiosulphate	3200	3100	4000	4100	3800	3600
Sulphate	5600	5800	4100	4300	3300	3260
Sulphite	660	600	450	480	260	300
Chloride	1020	1100	720	780	820	800

See text and Section 2 for other conditions.

Table 5
Comparison of CE and titrimetry results for sodium hydroxide (EA) in white, green and black liquors

Liquor sample	NaOH (mM)	
	CE	Titration
WL-A	2650	2700
WL-B	2240	2300
GL-A	850	880
GL-B	970	970
BL-A	280	300
BL-B	260	280

See text and Section 2 for other conditions.

were also analyzed before and after the addition of known amounts of sulphide, oxysulphur anions and chloride. As indicated in Table 4, the recoveries ranged between 99 and 115% for all anions studied.

3.1.6. Analysis of hydroxide by CE and titrimetry

The hydroxide present in pulp and paper industry samples is commonly referred to as the effective alkalinity (EA) of the liquor and is traditionally measured by classical titration methods [1,2,6,7]. Salomon and Romano were the first workers to demonstrate that hydroxide can be separated in kraft liquors by CE [26]. However, they did not demonstrate that it could be quantified using their electrolyte system.

As indicated previously [26] and as shown in this work, hydroxide gives a single peak, which elutes before all other analytes, which is consistent with the fact that has the highest net mobility of all anions. In the current work, we discovered that the concentration of TTAOH had a significant effect on the shape of the hydroxide peak in both standard solutions and in all three types of kraft liquors, as illustrated in Fig. 6. As indicated, the hydroxide peak obtained with the electrolyte containing 10 mM chromate and 2 mM TTAOH exhibits a peak shape that possesses considerable fronting, which is expected in CE separations when the analyte possesses a significantly higher mobility than that of the carrier ion (chromate). In contrast, the shape of the hydroxide peak obtained with an electrolyte containing 10 mM chromate and 0.5 mM TTAOH is more complex and does not exhibit the same peak shape as that seen when 2 mM TTAOH is present. Since the main differences in the two electrolytes is the concentration of TTAOH and thus the concentration of hydroxide (pH 11.8 for the former and 10.2 for the later electrolyte), it appears that one or both these parameters have a significant impact on the shape of the hydroxide peak. To our knowledge, there have not been any published reports describing the effect of electrolyte composition on hydroxide peak shape. Nor have there been any reports on the quantitative analysis of hydroxide in kraft liquors or any other type of sample by CE. At the time of writing this report, the observed changes in the hydroxide peak are not clearly understood.

In order to assess whether hydroxide could be quantified by our CE method, we analyzed all three types of liquors by both CE and classical titration methods. As shown in Table 5, the hydroxide results obtained by CE and titrimetry were found to differ by only about 3% in the samples studied. As pointed out earlier, the hydroxide result obtained by

Table 4
CE results from spike-recovery experiments for several anions in green and white liquors

Anion	Anion concentration (mg/L)			Recovery (%)
	Original (mean ± S.D.), $n = 3$	Added	Found (mean ± A.D.), $n = 2$	
GL-E				
Chloride	820 ± 40	400	420 ± 10	105 ± 3
Thiosulphate	3770 ± 50	4000	4320 ± 120	106 ± 3
Sulphide	11540 ± 250	2000	1980 ± 40	99 ± 2
Sulphate	3260 ± 120	4000	4160 ± 120	104 ± 3
Sulphite	260 ± 20	200	210 ± 10	105 ± 5
WL-D				
Chloride	960 ± 50	200	200 ± 2	100 ± 1
Thiosulphate	3430 ± 50	2000	2130 ± 30	106 ± 2
Sulphide	9310 ± 110	3000	3000 ± 90	100 ± 2
Sulphate	5830 ± 30	2000	2060 ± 40	103 ± 2
Sulphite	750 ± 70	200	230 ± 30	115 ± 15

Each sample was diluted and spiked with the concentration indicated below. Three replicate analyses were performed on the original samples, and the spikes were performed in duplicate. See text and Section 2 for other conditions. The average deviation from the mean is designated as A.D.

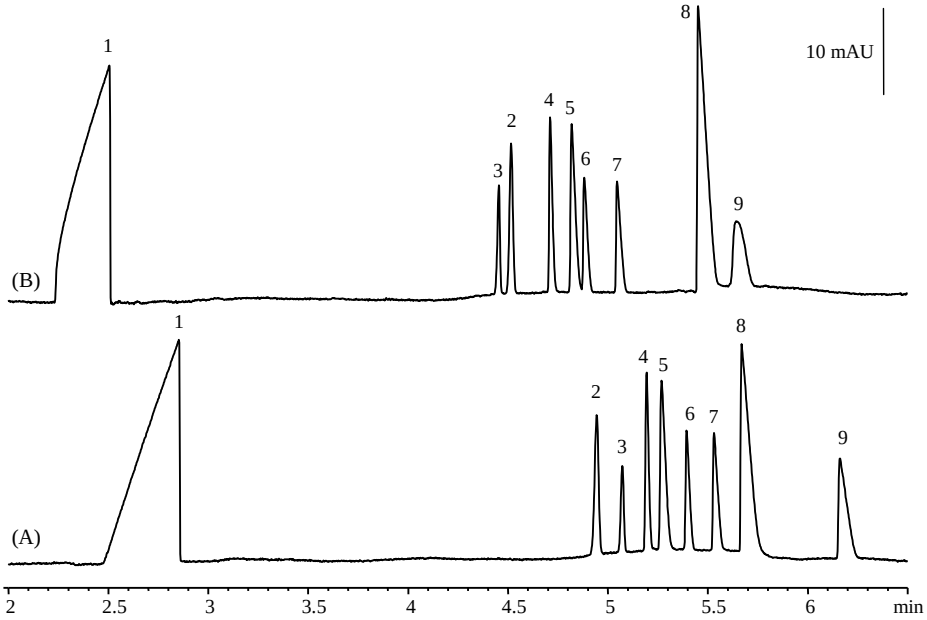

Fig. 6. Effect of electrolyte composition on hydroxide peak shape and on the order of migration of anions present in a standard mixture. Chromate concentration was constant at 10 mM but TTAOH was 2 mM (A) and 0.5 mM (B). Separation conditions and standard mixture composition as specified in Fig. 1. See text and Section 2 for further details.

CE is equivalent to the effective alkalinity (EA) of he sample, which is the result one obtains by the classical titration methods. The results indicate that CE can be used to accurately determine the EA content of kraft liquors in a much more convenient manner than is possible by conventional methods. The major advantage of the CE method is that very little sample preparation is required, no interferences occur and a direct measurement of the EA and other anion data, such as sulphide can be obtained in a single run.

3.1.7. Analysis of carbonate by CE and classical methods

During the course of this work it was discovered that the carbonate results obtained by the optimized CE method were 5–25% lower than those obtained by well established and validated methods such as IC and coulometry. After examining the literature, it was postulated that a phenomenon known as "reverse electrostacking" [25] may be responsible for the low carbonate results. Reverse electrostacking, as the name implies, is the opposite of electrostacking, which is a positive and desirable affect in CE analysis. Reverse electrostacking is defined as the migration of an ion (which is present in both the sample and the electrolyte) from the bulk electrolyte to the boundary between the sample zone and the electrolyte. The magnitude of reverse electrostacking increases with increasing sample ionic strength and occurs after the sample has been loaded, and an electrical field applied across the capillary. Since carbonate levels may vary considerably in the background electrolyte and because carbonate is an abundant in the samples studied in this work, it was thought that reverse electrostacking of carbonate may be responsible for the low result obtained in this study. In indirect photometric detection, reverse electrostacking manifests itself as an increase in the absorbance of the chromate in the region or zone where the electrolyte has been depleted in carbonate. This results in a baseline deflection opposite in direction to that produced by an analyte. Consequently, the net peak area observed for carbonate (which is actually due to a decrease in the absorbance of chromate which has been displaced by the carbonate anion) will be smaller than expected, and thus a low carbonate result will be observed.

The extent of reverse electrostacking should, therefore, be considerably reduced when the concentration of carbonate in the background electrolyte is minimized. The majority of carbonate present in the electrolyte enters as a contaminant in the TTAOH, but a small additional amount of carbonate also form during pressurization (injection) of the inlet electrolyte vial, via the reaction of atmospheric carbon dioxide with hydroxide present in the electrolyte. By minimizing the concentration of TTAOH used in the electrolyte, and by using fresh electrolyte for each analysis, the concentration of carbonate in the electrolyte and, therefore, the degree to which reverse electrostacking occurs, should be minimized.

This hypothesis was tested by performing carbonate analyses on standards and on samples of white and black liquor using two electrolytes, each containing 10 mM chromate but with different levels of TTAOH (2.0 and 0.25 mM). Plots of peak area versus carbonate concentration were linear over the range of 10–100 mg/L, with a correlation coefficient of 0.999 or better for both electrolytes. The R.S.D.s of the migration time and peak area were 0.2 and 2.5–3.5%, respectively, for a carbonate standard and a sample of white liquor, based on 4 replicate analyses. As indicated in Table 6, carbonate results obtained using the electrolyte with 0.25 mM TTAOH were in very good agreement with those obtained

Table 6
Comparison of carbonate results obtained for white, green and black liquors by IC, coulometry and CE

Liquor sample	Carbonate (g/L)			
	IC	Coulometry	CE (2 mM TTAOH)	CE (0.25 mM TTAOH)
WL-A	14.4	14.0	10.7	14.0
WL-B	19.4	19.4	14.6	19.3
GL-A	70.4	71.9	58.1	71.1
GL-B	79.3	81.8	62.5	82.1
BL-A	14.9	15.1	13.5	14.8
BL-B	10.2	10.4	9.0	10.0

Two electrolytes were used in the CE analyses. Both contained 10 mM chromate and the concentrations of TTAOH specified in the table. See text and Section 2 for other conditions.

by IC and coulometry, while results obtained with 2 mM TTAOH were significantly lower, presumably because of reverse electrostacking phenomenon. Unfortunately, the electrolyte optimized for the determination of carbonate is unsuitable for the analysis of chloride and thiosulphate because they co-migrate. Interestingly, we found that the carbonate peak was more symmetrical and migrated later when 0.25 mM TTAOH was used. The reason for the improved symmetry is currently unknown. The longer migration time for carbonate is due to the lower pH of the former electrolyte.

4. Conclusions

Several problems, which severely limited the analysis of anions in kraft liquors by CE, were identified and resolved. The improvements included optimizing the electrolyte composition, selecting a more suitable detection wavelength, conducting separations under constant current conditions and implementing a post run column cleaning protocol. In addition, quinones were identified as being responsible for catalyzing the oxidation of sulphide in black liquors during the sample dilution step prior to CE analysis. The addition of reduced glutathione during the dilution step was found to prevent sulphide oxidation and allowed for quantitative analysis of all sulphur species in black liquor. Results obtained by the new CE method were in good agreement with classical methods for all analytes of interest in kraft liquors. The new CE method provides a fast, convenient and unique approach for simultaneously determining EA, sulphur species, chloride, carbonate, formate and oxalate in kraft liquors.

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