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Rapid Analysis of Inorganic and Organic Anions in Kraft Pulping Liquors by Capillary Zone Electrophoresis

Joseph Sullivan

A Thesis

In

The Department

of

Chemistry and Biochemistry

Presented in Partial Fulfilment of the Requirements
for the Degree of Master of Science
Concordia University
Montreal, Quebec, Canada

June, 1998

0-612-39461-1

ABSTRACT

Rapid Analysis of Inorganic and Organic Anions in Kraft Pulping Liquors by Capillary Zone Electrophoresis

Joseph Sullivan

New methods have been developed for determining and/or speciating several important inorganic sulphur species, including: thiosulphate, sulphate, sulphite, sulphide and polysulphide in kraft pulping liquors and effluents by capillary zone electrophoresis. In addition, several other key anions, including: hydroxide, carbonate, oxalate, formate and chloride can be quantified in the same process liquors.

Two approaches were developed for determining the anions. In one method, anions were baseline resolved and quantified using sodium chromate, tetradecyltrimethylammonium hydroxide-based electrolytes with indirect UV-detection. In the second scheme, polysulphide was speciated, and sulphur species such as sulphide, thiosulphate and sulphite, as well as hydroxide were separated and determined using a sodium sulphate, tetradecyltrimethylammonium hydroxide-based electrolyte with direct UV-detection. A third approach, involving the use a 2-[N-Cyclohexylamino]ethanesulfonic acid, hexamethonium hydroxide electrolyte with conductivity detection was also briefly examined and found to be unsuitable for the analysis of sulphide-bearing samples.

Sulphide and several oxysulphur species were found to be relatively stable in standard solutions and in white and green liquors diluted in He-sparged water. However, sulphide was rapidly oxidized to sulphite and thiosulphate in dilute black liquor prepared in the same solvent. Studies using several model quinones showed that 1,4-benzoquinone and 2-hydroxy-6-methoxy-1,4-benzoquinone rapidly oxidize sulphide to sulphite and/or thiosulphate. Addition of reduced glutathione, a biologically important antioxidant, to solutions containing sulphide and the above mentioned quinones and to dilute black liquor samples prepared in He-sparged water, was extremely effective in stabilizing sulphide. In both cases, sulphide was found to be stable for more than one hour at room temperature. The findings suggest that the oxidation of sulphide in dilute black liquor is largely due to oxygen-mediated redox reactions between quinones and sulphide. The results also suggest that efficacy of glutathione in stabilizing sulphide may be due to its ability to act as a free radical scavenger.

Sample ionic strength and reverse electrostacking were found to be important factors affecting the reliability of the determination of carbonate by indirect detection. Strategies for overcoming these problems are presented. The validity of the CE method was verified by comparing CE results with those obtained by ion chromatography, titrimetry and/or potentiometry, and from spike-recovery experiments.

ACKNOWLEDGEMENTS

I am indebted to my supervisors, Drs. Maurice Douek, Peter Banks and Susan Mikkelsen for their encouragement, advice, guidance and support during the course of my graduate studies and during my work on this research project.

I wish to thank Dr. Douek for providing me with the opportunity and resources to conduct my research work at the Pulp and Paper Research Institute of Canada. You have been a great mentor.

A special thanks to my wife, Linda and my sons, Lynus and Davin, for their unwavering support, understanding and love over the years. Each of you made great sacrifices so that I could pursue graduate studies.

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CHAPTER 1

INTRODUCTION

1.1 Pulp and Paper Manufacture

While the use of computers and other electronic communication devices has increased over the last decade, paper continues to be the primary means of recording, storing and disseminating information. Pulp is a major component in the manufacture of paper and paperboard. Pulp is the generic term for a wide range of products resulting from the manufacturing processes that involve the chemical and/or mechanical treatment of various types of plant material. Wood currently provides the basis for approximately 90 percent of global pulp production. The remaining 10 per cent is derived from straw, bamboo, bagasse, kenaf, flax, hemp and cotton. In 1996, Canada ranked second in the world in terms of total wood pulp production. During the same year, Canada produced a total of 24.4 million tonnes, with 9.9 million tonnes valued at $6.5 billion delivered outside the country.

1.2 Wood Chemistry

Wood is a highly heterogeneous material, composed of cellulose, hemicelluloses, lignin, lipophilic extractives and small amounts of inorganic species, including chloride, phosphate, carbonate, salts of alkali, alkaline earth and certain transition elements. Cellulose is the main constituent of wood. It is a homopolymer comprised of β-D-glucopyranose units linked together by (1→4)-glycosidic bonds. Hemicelluloses are a group of heterogeneous, often extensively branched polysaccharides that are comprised of the monosaccharides D-glucose, D-mannose, D-xylose, L-arabinose, D-galactose and small amounts of L-rhamnose in addition to D-glucuronic acid, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid.

Lignins, are highly polymerized substances consisting of phenylpropane units, which act as a "glue", imparting structural rigidity to wood. More than two thirds of the phenylpropane units in lignin are linked by ether bonds, the rest by carbon-carbon bonds. Lignins are linked primarily to hemicellulose components in wood. Wood extractives include a broad range of low molecular weight compounds which can be extracted from wood with organic and/or aqueous solvents. Consequently, extractives are comprised of both lipophilic and hydrophilic compounds. The lipophilic compounds include several phytosterols, glycerides, fatty and resin acids, terpenoids and alcohols. The hydrophilic compounds include several mono- and oligosaccharides, flavones, flavanoids, and aryl and alkyl-substituted phenols. The chemical composition and relative distribution of the various components present in wood is shown in Figure 1.1 [1]. Inorganic species are not shown in the figure, since they typically make up less than 1% of the wood. The chemical structure of lignins is illustrated in Figure 1.2 [2].

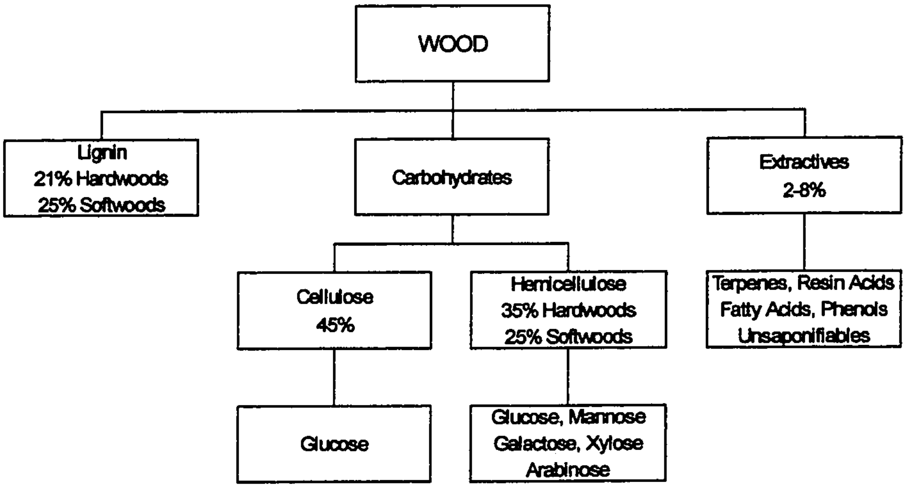
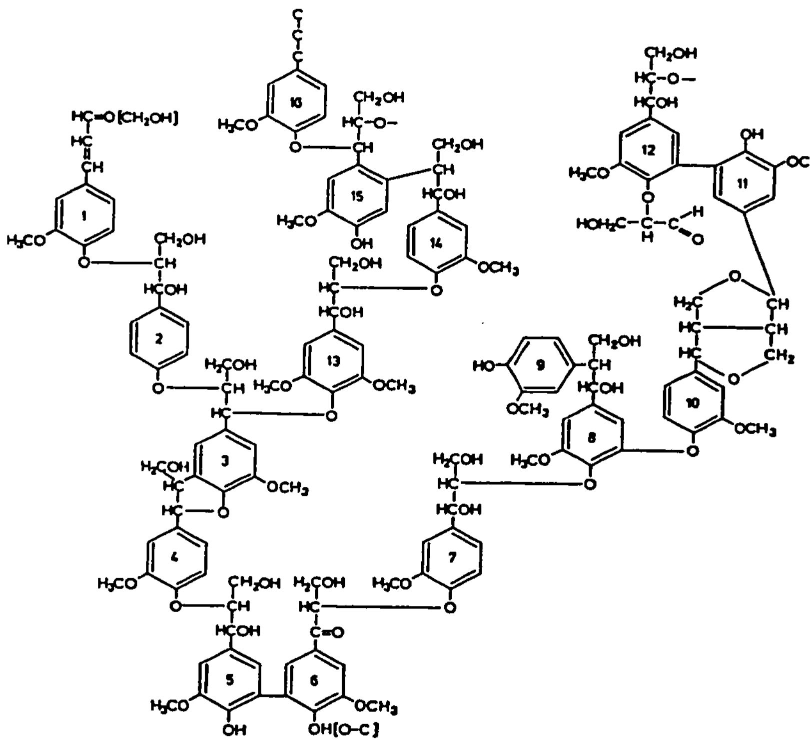


Figure 1.1 The chemical composition of wood.



Group[a]	Spruce lignin	Birch lignin
Methoxyl	92-96	139-158
Phenolic hydroxyl (free)	15-30	9-13
Benzyl alcohol	15-20	
Noncyclic benzyl ether	7-9	
Carbonyl	20	

[a] The contents may vary depending on the origin of the lignin (e.g., middle lamella or secondary wall lignin).

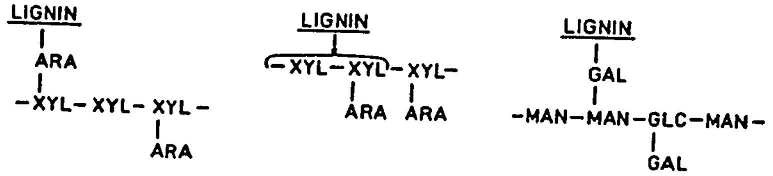


Figure 1.2. Prominent structures of softwood lignin comprising 16 phenylpropane units (top); the functional groups of lignin per 100 C_9 units (middle); and examples of the linkages between lignin and hemicelluloses (bottom). The designations ARA, XYL, GLC, MAN and GAL refer to arabinose, xylose, glucose, mannose and galactose, respectively.

1.3 Kraft Pulping

The first step in making paper involves the liberation of fibres from wood residues via pulping. Pulping may be accomplished through mechanical, chemical or a combination of both processes. Kraft pulping is one of the major chemical processes used to convert wood-based lignocellulose into cellulosic fibres. Kraft fibres are used extensively in paper making because they possess a number of desirable physical and optical properties, such as high mechanical strength and high brightness (low lignin content), which make them suitable for the production of high quality unbleached and bleached pulp and paper products [1]. In 1996, kraft pulp accounted for 108 of the 160 million metric tons or 68% of the total pulp produced globally.

The main objective of the kraft pulping process is to degrade and dissolve away the lignin and leave behind most of the cellulose and hemicelluloses in the form of intact fibres. To achieve this, the bonds within the insoluble cross-linked lignin and those between lignin and carbohydrates must be broken so that the lignin can be solubilized and removed from the individual fibres. In kraft pulping, wood chips undergo extensive delignification when heated (cooked) at temperatures of up to 180°C in the presence of an aqueous solution of inorganic reagents known as white liquor (WL). Industrial white liquor consists primarily of NaOH, Na_2S and increasingly Na_2SS_n (sodium polysulphide, where $4 \geq n \geq 1$), along with variable concentrations of $Na_2S_2O_3$, Na_2SO_3, Na_2SO_4, Na_2CO_3 and NaCl [3-5]. The active components in the WL responsible for delignification are the hydroxyl, sulphide and polysulphide ions [5]. At the end of the digestion, about 80% of the lignin, 50% of the hemicellulose and 10% of the cellulose originally present in the wood has been dissolved in the spent white liquor, and a large portion of the alkali (hydroxide), sulphide and polysulphide have been consumed through acid-base, hydrolysis, substitution and redox reactions with the wood components. At this point in the process, the spent white liquor is referred to as weak black liquor (WBL). Weak black liquor is a complex mixture containing hundreds of compounds, including low and high molecular weight lignin fragments, phenolic compounds, carbohydrates, organic acids and several inorganic species. The total content of dissolved solids present in WBL is 10-20% (w/w).

To ensure the economic viability of the kraft process, it is necessary to recover the carbon, sulphur and sodium present in the WBL. This is done by first concentrating the WBL in an evaporator followed by incineration of the resultant strong black liquor (SBL) in a furnace. During incineration, energy in the form of steam is generated from the combustion of the organic compounds and the important inorganic compounds present in the SBL are recovered as molten Na_2S and Na_2CO_3 (smelt). The smelt is dissolved in water to form green liquor (GL) which is then reacted with quick lime ($Ca(OH)_2$) to convert Na_2CO_3 into NaOH and thus regenerate the original white liquor (Na_2S + NaOH). As mentioned earlier, industrial WL contains appreciable levels of impurities (non essential inorganic ions) such as chloride, sulphate, thiosulphate and carbonate. The sources of the major anionic impurities, such as oxysulphur ions and carbonate, arise from inefficiencies in the recovery process, while chloride originates from the make up chemicals and the wood. The various steps involved in recovery and conversion of the kraft cooking chemicals is illustrated in Figure 1.3 [2].

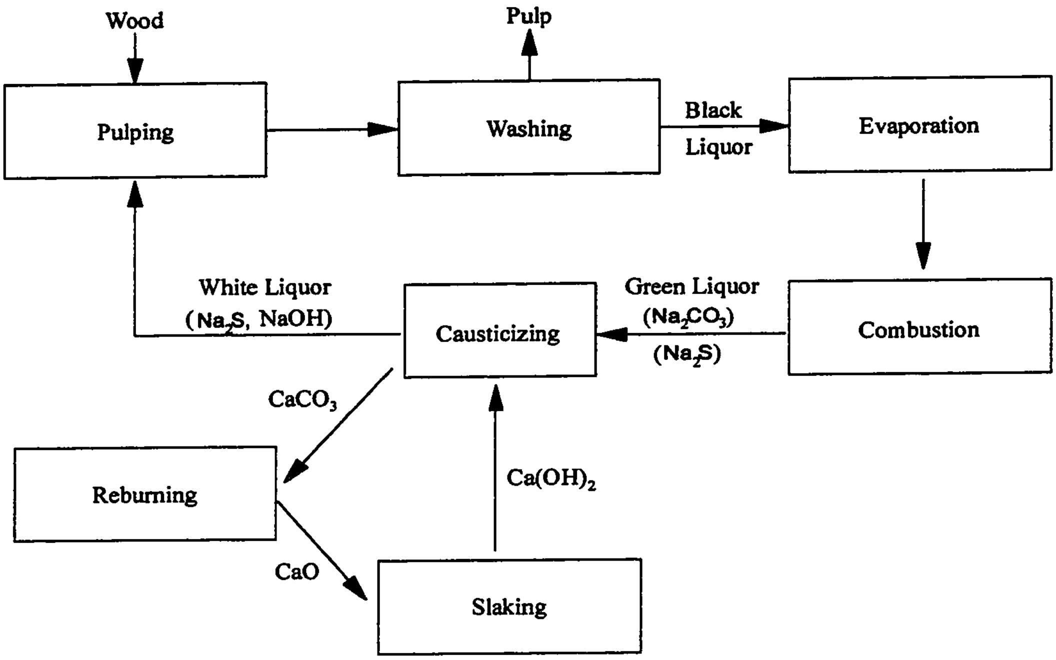


Figure 1.3. Recovery and conversion of kraft cooking chemicals.

1.4 Overview of Conventional and Modern Methods for the Determination of Hydroxide and Sulphur Species

1.4.1 Classical Methods

Careful monitoring and control of the composition of the various pulping 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/gravimetric methods for determining hydroxide, carbonate, sulphide, sulphite, sulphate and thiosulphate in white and green liquors, have been developed and used for more than 40 years [6-8]. However, these methods 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.

More recently, complexometric, potentiometric and/or conductimetric methods have been developed for determining residual alkali and sulphide in black liquor [9-12]. However, these methods are somewhat limited in scope and are not suited to the analysis of all of the species of interest.

1.4.2 Modern Instrumental Methods

Ion chromatography (IC) has become a widely accepted technique for the determination of the major inorganic sulphur anions in kraft process liquors [13-15]. 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/or detectors. 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 that IC methods, they are prone to interference when complex samples such as black liquor are analysed and/or 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 [16,17], while a second method employs colorimetry to determine sulphide only. [18]. The main advantage of FIA over IC is that an expensive column is not used.

On-line methods utilizing Fourier transform infrared (FT-IR) spectroscopy with attenuated total reflectance (ATR) and near infrared (NIR) transmittance spectroscopy have been recently developed for determining sulphide, alkalinity and chloride in kraft liquors [19,20]. These approaches use partial least-squares (PLS) multicomponent calibration techniques to build spectral models for the analytes of interest. The methods have proven very useful for determining total alkalinity, sulfide 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, these approaches are quite limited in the number of analytes that can be determined and the types of samples that can be analysed, 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.

1.5 Overview of Capillary Electrophoresis

Electrophoresis is a well-established technique for separating solutes based on differences in their electrophoretic mobility under the influence of an applied electric field [21]. Capillary electrophoresis (CE) is a form of electrophoresis that dates back to the late 1950s. While the concept of CE has been known for some time, it was not until 1967 that the first prototype CE apparatus and the concept of "Free Zone Electrophoresis" was described by Hjertén [22]. This work led to the development of numerous forms of CE including: capillary zone electrophoresis (CZE), micellar electrokinetic chromatography (MEKC), capillary gel electrophoresis (CGE), capillary isoelectric focusing (CIEF), capillary isotachophoresis (CITP) and capillary electrochromatography (CEC). Over the last decade, CE has developed into a powerful analytical technique, primarily because of the availability of high quality capillaries and sophisticated, commercially available instrumentation. In addition, the development of sensitive detectors suitable for use in CE has aided in the acceptance and utility of the technique. A common factor among all forms of CE is that separations are performed in narrow-bore fused silica capillaries. Detection methods employed include: Indirect and direct UV-visible absorption, conductivity, fluorescence, laser-induced fluorescence (LIF), electrochemical and mass spectrometry (MS). 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 analyse complex samples with little sample preparation; and the ability to use relatively inexpensive capillary columns for most separations. Fundamental reviews of the state of the art of CE have been published recently [23,24].

1.5.1 Capillary Zone Electrophoresis

Among the various forms of CE, CZE is the simplest and most widely used. In CZE, as in most other forms of CE, solutes are separated in electrolyte-filled capillaries having internal diameters of 25-100 μm, external diameters of 150-380 μm and lengths ranging between 25-100 cm. As Illustrated in Figure 1.4, the basic CE instrument consists of a high voltage power supply capable of delivering 0-30 kV, a polyimide-coated fused silica capillary, two electrolyte reservoirs, into which the capillary and electrodes are suspended, and a detector which is placed near the outlet end of the capillary.

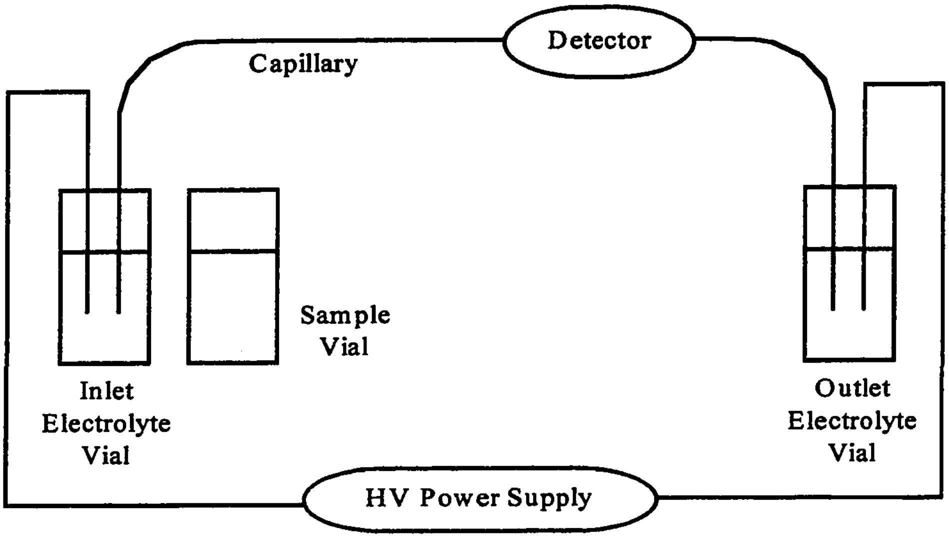


Figure 1.4. Basic components of a capillary electrophoresis instrument.

When the capillary is filled with an electrolyte with a pH > 2-3, the acidic silanol groups on the inner wall of the capillary are ionized and exist as negatively charged sites. Counter ions remain in the vicinity of this surface to maintain charge balance. The counter ions form a double layer and create a potential difference known as the zeta-potential, close to the wall. The zeta-potential, denoted by ζ, is given by the Helmholtz equation,

$$\zeta = \frac{4\pi\eta\,\mu_{EOF}}{\epsilon} \qquad (1)$$

where η is the viscosity, μ_{EOF} is the electroosmotic mobility and ϵ is the dielectric constant of the electrolyte. The thickness of the double layer, designated as $1/\kappa$, is determined by the ionic strength of the electrolyte, according to the Debye-Huckel theory.

$$\frac{1}{\kappa}, nm = \frac{1}{3.288\sqrt{ionic\ strength}} \tag{2}$$

For electrolytes with concentrations ranging from 10^{-1} to 10^{-4} M, this thickness is from 1 to 30 nm. Under the influence of the applied field, counter ions near the inner surface of the capillary are drawn toward the cathode. Because these cations are solvated, their movement also drags the bulk solution in the capillary towards the cathode, resulting in an electroosmotic flow (EOF) of electrolyte. Since the zeta potential is determined by the charge on the inner surface of the capillary wall, and since this charge is strongly dependent on the pH, the magnitude of EOF (μ_{EOF}) varies with pH.

The first step in any analysis is introduction of sample into the capillary. This can be done, by replacing the inlet vial with a sample vial and then applying an electric field, or an external pressure or by elevating the sample vial relative to the outlet vial producing a siphoning action. After loading the sample, the inlet vial is replaced with an electrolyte vial and an electrical potential of up 30 kV is applied across the capillary. In CZE, the "normal polarity" across the capillary is inlet or anode positive (+) and outlet or cathode negative (-). During electrophoresis, anions migrate toward the anode, while the cations migrate toward the cathode. Neutral species migrate with the same velocity as the EOF. Because the magnitude of the EOF is typically much greater than the electrophoretic mobility of the anions, all species, including anions, are swept by the EOF toward the cathode. Cations elute first, followed by neutral species and finally anions. The electrophoretic mobility of a species (μ_a) can be approximated by the Debye-Huckel-Henry theory,

$$\mu_a = \frac{q}{6\pi\eta r} \tag{3}$$

where q is the charge on the particle, η is the viscosity of the electrolyte and r is the Stoke's radius of the particle. The mass of the particle may be related to the Stoke's radius by $M = (4/3)\pi r^3/V$, where V is the partial specific volume of the solute. From the above relationships, it is evident, that in general, solutes with high charge and small radii (large hydrodynamic volumes) will thus exhibit the highest mobilities in an electric field. The velocity (v_a) of a solute in the electric field is given as follows,

$$v_a = \mu_{app}E = (\mu_a + \mu_{EOF})E \tag{4}$$

where μ_{app} is the vector sum of the solute and electroosmotic mobilities and E is the applied electric field strength in (V/cm). The migration time (t) of a solute is then obtained by the following relationship,

$$t = \frac{L_d}{\mu_{app}E} \tag{5}$$

where L_d is the effective capillary length to the point of detection. The theoretical plate number (N) can be determined directly from the electropherogram using equation 6.

$$N = 5.54\left(\frac{t}{w_{1/2}}\right)^2 \tag{6}$$

The resolution (R_s), between two adjacent peaks can be calculated from equation 7,

$$R_s = \frac{2(t_2 - t_1)}{(w_1 + w_2)} \tag{7}$$

Where, in equations (6) and (7), the t values refer to the migration times of two solutes in minutes and the w values correspond to the baseline widths of the peaks in minutes.

1.5.2 Application of CZE to the Analysis of Low Molecular Weight Inorganic and Organic Anions [25-27]

The earliest inorganic anion separations by CZE were reported by Mikkers et al. and Gebauer et al. in 1979 and 1983, respectively [28,29]. Solutes were detected using UV and/or conductivity detection. In 1990, Jones and Jandik showed that high efficiency, high speed separation of anions was possible using a chromate electrolyte containing an EOF modifier with indirect UV-detection. In their approach, an alkyl quaternary amine (cationic surfactant) is added to the electrolyte. The cationic portion of the surfactant ion-pairs with the ionized silanols such that their hydrophobic chains are oriented toward the fluid in the capillary. When the surfactant is present at concentrations below the critical micelle concentration (CMC), additional tail-to-tail pairing between the adsorbed surfactant and free surfactant occurs, resulting in the formation of hemicelles (or bilayer) near the inner surface of the capillary wall. The net result is a reversal of the charge (from negative to positive) on the inner surface of the capillary and a concomitant reversal of the EOF. By using a negative polarity at the inlet of the capillary and reversed EOF, a so called co-EOF condition is achieved. In essence, both anion migration and electrolyte flow are toward the detector. The result is reduced analysis times with minimal dispersion due to longitudinal diffusion, and thus very efficient separations.

Because most of the inorganic anions (and cations) do not possess a chromophore or fluorophore, indirect photometric detection (IPD) is used. For IPD, the electrolyte is chosen so that it contains a UV absorbing co-ion. In IPD, the detector measures the absence of the co-ion which is physically displaced charge-for-charge by the analyte ions. Consequently, the co-ion must possess at least one unique UV absorption maxima in a region that is not shared by the analytes. In addition, the co-ion should have a mobility (ionic equivalent conductance) similar to that of the analytes in order to obtain symmetrical peaks. Moreover, the co-ion must be stable (unreactive) towards the analytes under the conditions of the analysis. The faster (more mobile) the analyte is compared to the co-ion, the more the analyte fronts. Conversely, the slower (less mobile) the analyte is compared to the co-ion, the more the peak will tail. For capillaries with 75 μm internal diameters, Jones and Jandik showed that chromate (as co-ion) provides optimal peak symmetry with inorganic anions, but carboxylates (low mobility ions) give tailing peaks. However, they subsequently found that symmetrical peaks could be obtained for both inorganic and carboxylate anions using the chromate electrolyte and a 50 μm i.d. capillary. In many applications, it is desirable to use an electrolyte that possesses the lowest conductivity possible, along with high ionic strength and high buffering capacity so that joule heating is minimized and sample stacking is maximized, without adversely affecting the separation. These characteristics also ensure that the electrolyte will be less susceptible to degradation and/or alteration arising through electrolysis.

1.6 Thesis Organization

This thesis describes the development of new capillary zone electrophoresis methods for separating and quantifying a broad range of inorganic sulphur anions, and several other inorganic and organic anions in complex process liquors from the kraft pulp and paper industry. In addition, a new method for speciating inorganic polysulphide in highly alkaline samples is described.

In the course of this work, several new findings on the chemistry of sulphide were made. Sulphide was found to be very unstable in lignin-rich samples that had been diluted for analysis, and this instability was found to compromise the validity of the analytical results not only for sulphide, but for several other key sulphur species as well. It was discovered that sulphide undergoes oxygen-mediated redox reactions with certain quinones and/or quinone moieties within the lignin found in these samples. A suitable reagent, namely reduced glutathione, was found to completely stabilize sulphide in dilute samples for up to one hour. Consequently, it became possible to reliably quantify the sulphur analytes of interest. The discoveries in this work represent a major advance in the ability to simultaneously analyse several anions using a single set of conditions.

Chapter 2 focuses on an evaluation of a commercial conductivity detector for the analysis of sulphide-bearing samples.

Chapter 3 describes the development of a method for determining the major inorganic sulphur species and a number of other anions in kraft pulping liquors using CE with indirect detection. Studies on the cause of sulphide instability in lignin-rich samples, as well as the development of a simple method for stabilizing sulphide in these samples using reduced glutathione are presented. Finally, an assessment of the quantitative nature and validity of the CE method is made by comparing CE results with those obtained by ion chromatography, titrimetry and/or potentiometry, and from spike-recovery experiments.

Chapter 4 is concerned with the development of a method for speciating polysulphide and for determining hydroxide, thiosulphate, sulphide and sulphite in highly alkaline samples using direct UV-detection. The validity of the CE method was assessed by comparing CE results with those obtained by titrimetry and/or potentiometry, and from spike-recovery experiments.

Chapter 5 is a summary of the results presented in Chapters 2-4 and presents suggestions for future work.

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CHAPTER 2

EVALUATION OF CAPILLARY ELECTROPHORESIS WITH CONDUCTIVITY DETECTION FOR THE ANALYSIS OF SULPHIDE-BEARING SAMPLES

2.1 Introduction

Traditionally, ionic species have been determined by ion chromatography (IC) with conductivity detection [1]. However, in recent years, capillary electrophoresis (CE) has become an important analytical tool for the analysis of small inorganic and organic ions [2-4]. Most of the CE methods developed to date utilize indirect photometric detection (IPD) for ion analysis. While IPD is a universal mode of detection, it suffers from relatively poor sensitivity. In IPD, a background electrolyte (BGE) is chosen such that it possesses a high absorptivity at a wavelength (typically in the UV) where the analytes are transparent. Analytes which migrate into the electrolyte displace the electrolyte on a charge-for-charge basis producing a decrease in the absorbance which is proportional to the concentration of the analyte. Detection limits in CE using IPD are in the 100-500 ppb level range for inorganic anions such as chloride and sulphate. This is at least one tenth of the sensitivity obtained with IC with suppressed conductivity detection. One approach to overcoming this problem has been to attempt to use extended light path capillaries. While this approach is very effective in direct UV applications it has proven very much less effective when using indirect detection. Other techniques such as electrokinetic sample injection are limited in that 1) injections are biased toward more mobile ions, and 2) the technique is limited to high purity low conductance water samples, as the rate of loading is inversely proportional to the sample conductivity.

Recently, one CE manufacturer has attempted to address the issue of poor sensitivity by developing a conductivity detector for use in their line of CE instruments [5,6]. The detector, which is based on the design by Huang et al. [7,8], monitors the conductivity difference between the sample zone and the background electrolyte using a disk electrode positioned ca. 25 μm from the end of the capillary. Prior to the introduction of this new detector, only a few reports on the use of conductivity detection with CE had been published [9-12]. However, all these detectors were custom-made or prototype cells. Some of the attractive features of conductivity detection, include: 1) high sensitivity for inorganic ions, and 2) the ability to use high ionic strength, low conductivity and highly buffered electrolytes. In principle, the resultant electrolyte formulations enhance sample stacking, are resistant to electrolysis effects and provide more reproducible separations.

To date, there have been no publications on the determination of inorganic sulphur species in pulp and paper process liquors using CE with conductivity detection. In this work, we report on an evaluation of a commercially available CE with conductivity detection for the analysis of sulphide-bearing, pulp and paper mill samples.

2.2 Experimental

2.2.1 Materials

2.2.1.1 Chemicals

Analytical grade sodium sulphide nonahydrate were obtained from Mallinckrodt (St. Louis, MO, USA). Sodium hydroxide, sodium sulphite, sodium sulphate, sodium thiosulphate, sodium chloride, sodium oxalate, sodium formate were ACS reagent grade or better and were from Aldrich (Milwaukee, WI, USA). Hexamethonium Bromide (HMBr), lithium hydroxide monohydrate, 2-[N-Cyclohexylamino]ethanesulfonic acid (CHES) were ACS-grade reagents from Sigma (St. Louis, MO, USA). Water used throughout this work was from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2.1.2 Apparatus

Studies were performed with a Crystal 310 CE instrument equipped with a Crystal 1000 CE conductivity detector, ConCap I capillary (50 cm x 50 μm i.d. x 375 μm o.d.) and a ConTip I sensor, all from Thermo Bioanalysis (Franklin, MA, USA). Instrument control and data acquisition were conducted using Thermo Bioanalysis software (version 1.3 beta) and the 4880 data acquisition package (version 3.0). The data acquisition rate was set to 20 Hz. All separations were performed at ambient room temperature using a constant voltage of -22 kV. All sample were injected using a pressure of 25 mBar for 12 seconds.

2.2.2 Methods

2.2.2.1 Electrolyte Preparation

The background electrolyte used for conductivity detection was comprised of 100 mM CHES, 40 mM $LiOH \cdot H_2O$ and 3 mM hexamethonium hydroxide (HMOH). Running electrolyte (250 mL) was prepared daily by diluting known weights of CHES, $LiOH \cdot H_2O$ and an appropriate volume of 25 mM HMOH in Milli-Q water.

A stock 25 mM HMOH solution (100 mL) was prepared by converting the bromide-form of the surfactant (HMBr) to the hydroxide-form using the following procedure: Approximately 125 mL of an aqueous 20 mM HMBr solution was allowed to flow under gravity through a 60 mL polypropylene syringe containing ca. 40 mL of washed Dowex-1 resin (Nuclear grade, OH-form, 100 mesh, Sigma Chemical Co., St. Louis MO). The last 100 mL of eluate was collected and stored in a 125 polypropylene bottle (Nalgene) at room temperature. Prior to use, the Dowex-1 resin was washed with 50 mL of 1M NaOH and 150 mL of Milli-Q water.

2.2.2.2 **Capillary Cleaning Protocol**

Initially each day, the capillary was washed with 0.5 M NaOH and water for 10 and 5 minutes, respectively. Prior to each analysis, the capillary was rinsed with electrolyte for 3 minutes. After each analysis, the capillary was washed with 0.5 M NaOH and twice with water (using separate vials) for 3, 2 and 1 minute, respectively. 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 capillary washes were performed using a pressure of 2000 mBar.

2.2.2.3 **Standards and Solutions**

A standard sulphide solution (ca. 1000 mg/L) was prepared weekly. The following procedure was followed to minimize the oxidation of sulphide during the preparation and storage of standards. Solid $Na_2S{\cdot}9H_2O$ was rinsed with water to remove oxysulphur species such as thiosulphate which may be present on the surface of the crystals. This can be done by grasping a crystal of the approximate mass required with a pair of tweezers and rapidly rinsing the crystals with a small quantity of He-sparged water, followed by immediate drying with a kimwipe. The dry, water-washed $Na_2S{\cdot}9H_2O$ crystal was transferred directly into a dry, tared, volumetric flask and He-sparged water was added to the mark. The sulphide crystals were allowed to dissolve without mixing or agitating the flask. After dissolution was complete, the contents of the flask were mixed gently by inverting the flask two or three times. The stock solution was not mixed again thereafter and was stored at 25 °C in the dark. Using these precautions, thiosulphate-free sulfide stock solutions were obtained. Dilute standards were prepared daily by dilution of stock sulphide with He-sparged water.

Stock sulphite solution (ca. 1000 mg/L) was prepared daily using the following procedure. A 250 mL volumetric flask was filled with 240 mL of 10 % (v/v) isopropanol in He-sparged water. An appropriate mass of sodium sulphite was placed in a small polypropylene weighing boat and transferred to the volumetric flask with small portions of 10 % isopropanol/water and diluted to volume with the same solvent. To avoid oxidation of sulphite, it is imperative that the flask not be agitated or mixed until the reagent is 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. Using these precautions, sulphate-free sulphite solutions were obtained.

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 six months when stored in the dark at room temperature.

Dilute mixed standards containing various combinations of ions were prepared daily by combining aliquots of the various stock solutions followed by dilution to volume with He-sparged water. It was found that sulphide and sulphite were stable in the mixed standards over the course of the day. All solutions and samples were prepared and stored in polymethylpentene (PMP) flasks (Fisher Scientific).

2.2.2.4 **Preparation of Samples**

Samples of black liquors were obtained from several Canadian kraft mills and stored at 4°C. Black liquor samples were prepared for analysis by first filtering ca. 5 mL of undiluted sample through 25mm x 5μm PTFE membrane syringe filters (Chromatography Sciences Company (CSC), St. Laurent, QC) into 5 mL polypropylene screw cap vials. The sample was then diluted in He-sparged water, and analysed immediately.

2.3 Results and Discussion

To date, the use of CE with conductivity detection has been limited to the analysis of non-sulphide bearing samples [5-13]. In addition, much of the previous work has been done with custom-built detectors, which were quite different in both design and operation from the detector used in the current work. Moreover, no attempt was made in previous studies to validate the methods employed. Consequently, it was not clear from the previous work whether CE with conductivity could be used for quantitative analysis, nor had it been established that sulphide and other anions could be determined in kraft process liquors. The first step in our work involved the analysis of a standard mixture of anions followed by the analysis of kraft black liquor.

2.3.1 Analysis of Anion Standards

Figure 2.1 shows the separations of anion standards using an electrolyte developed by Jones et al. [5]. The lower trace was obtained for a solution containing 5 mg/L each of chloride, thiosulphate, sulphate, oxalate, sulphite and formate. The upper trace was obtained with a mixture containing all of the previously mentioned species plus sulphide. As indicated in both traces, all anions are well resolved in about 6 minutes. However, it is evident from the upper trace, that the sulphide peak is severely attenuated and that the signal drops below the baseline after the peak apex. It is also evident that 20-30 seconds elapsed before the signal returned to its original value. These results indicate that sulphide is being adsorbed and/or degraded during the analysis.

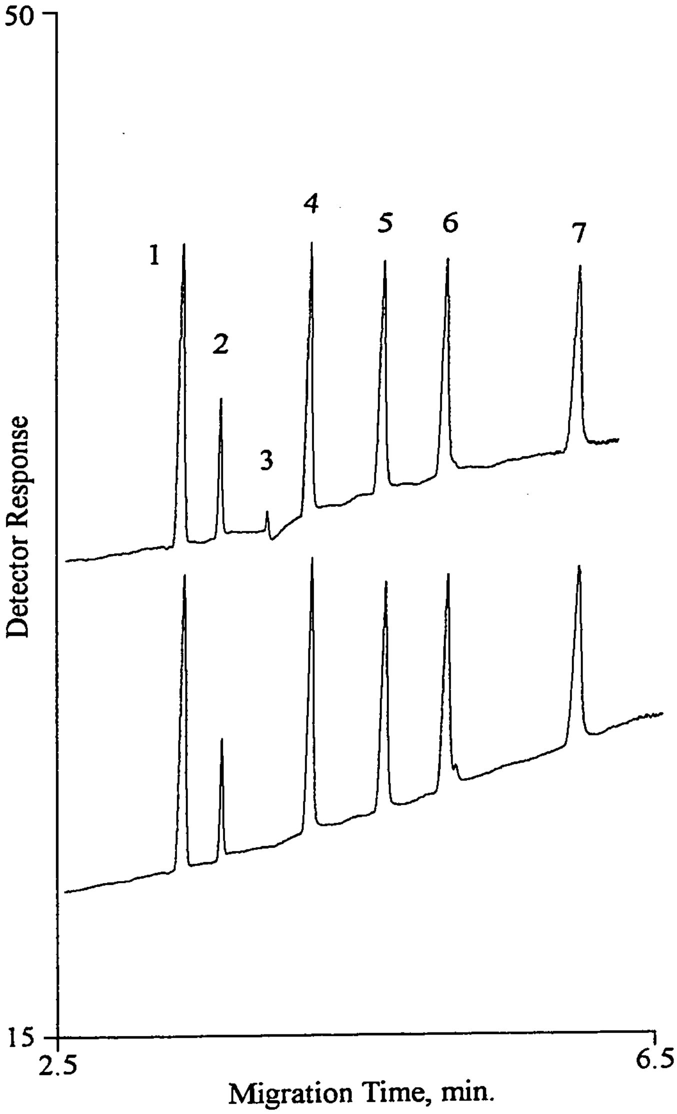

Figure 2.1. Separation of anions in standard mixtures. The upper trace was obtained with a mixture containing 5 mg/L each of chloride (1), thiosulphate (2), sulphide (3), sulphate (4), oxalate (5), sulphite (6) and formate (7). The lower trace was obtained with the same mixture, except that sulphide was absent. See Experimental for analytical conditions.

It was strongly suspected that sulphide was adsorbing to the outlet end of the ConCap and/or ConTip sensor or perhaps to the detector housing, since these components are fabricated in part from steel. The main components of the CE instrument are shown in Figure 2.2. A detailed view of the detector cell is outlined in Figure 2.3. It is well know that sulphide interacts strongly with many transition elements to form insoluble or sparingly soluble metal sulfides. In our work, sulphide may be lost through a reaction with the iron present in the steel components present in the detector to form iron sulphide (FeS or Fe_2S_3). To test this hypothesis, the ConTip sensor and ConCap capillary were removed from the cell block and inspected with the aid of a microscope.

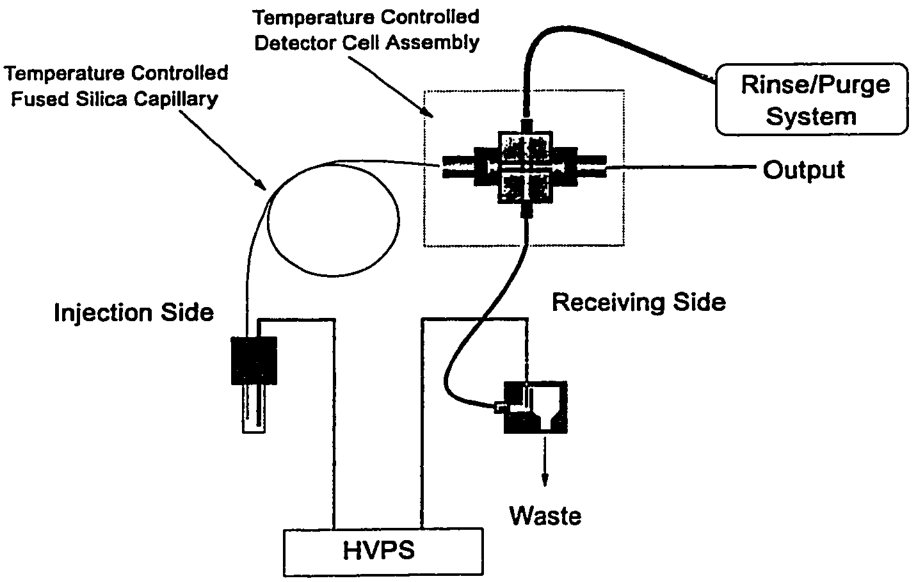

Figure 2.2. Basic components of the crystal 310 CE instrument equipped with a crystal 1000 conductivity detector [5,6].

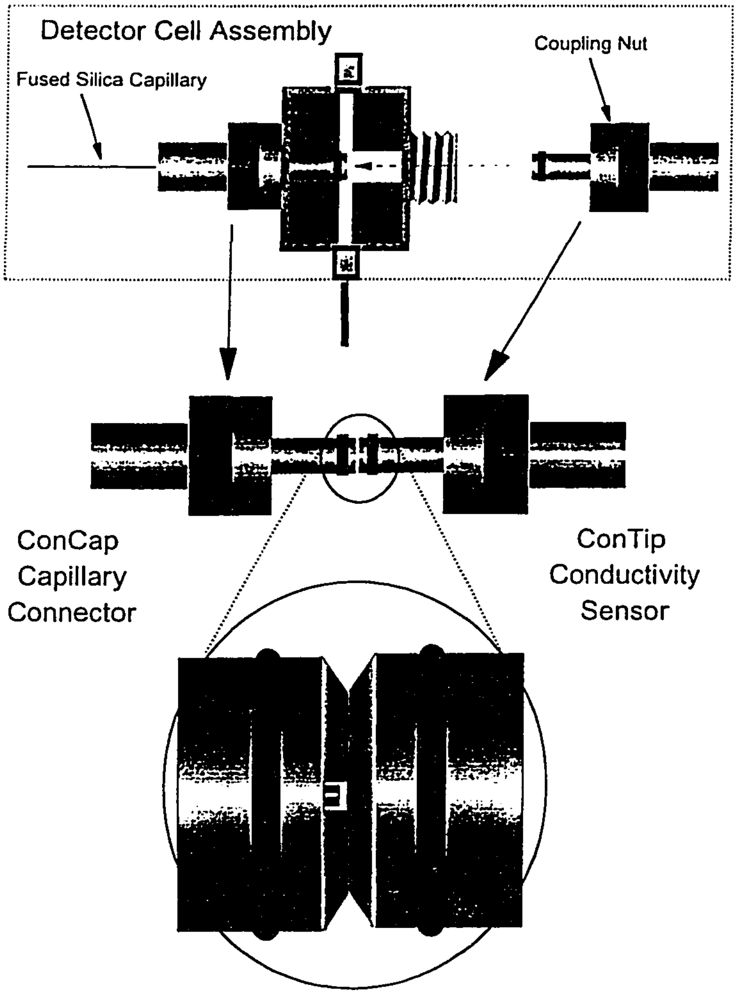

Figure 2.3. Detailed view of the components housed within the detector cell assembly [5,6].

The examination revealed the presence of a black deposit within the channels of the ConCap connector and a small amount of black deposit on the surface of the ConTip sensor as well. The presence and colour of the deposit are consistent with the appearance of iron sulphide and strongly support our hypothesis concerning the area in which sulphide loss is occurring. Once formed, the deposits within the ConCap are largely inaccessible and no simple and effective (non destructive) cleaning procedure was developed to deal with this problem. The only remedy for the problem was replacement of the ConCap unit. This was necessary because the capillary is permanently mounted in the ConCap connector, which is a fibre-optic type fitting, that serves to align the effluent end of the capillary with the conductivity electrodes found on the similarly designed ConTip conductivity sensor. The cost of replacing the ConCap unit is 150-200 $US.

Using a new ConCap, the repeatability of peak area and migration time for a standard mixture of anions (excluding sulphide) were determined. As indicated in Table 2.1, the percentage relative standard deviations (% RSDs) for peak areas ranged between 0.2 to 0.9% and from 1-2% for migration times. The linearity of the detector response for the same anions was determined over the concentration range of 1 to 50 mg/L. As indicated in Table 2.2, the detector response for each ion was linear over the concentration range studied, with correlation coefficients of at least 0.993 for each ion. The results suggest that materials within the conductivity detector are unsuitable for determining sulphide, but may be acceptable for measuring most other common anions. It was found that by adding an excess of a transition element (such as Cd in the form of the acetate salt) to a standard solution of anions, including sulphide, no peak for sulphide was obtained, indicating that sulphide was precipitated as CdS.

Table 2.1. Repeatability of migration time and peak area for a standard mixture of anions. The mean values were obtained from 6 replicate injections of a standard mixture containing 1 mg/L of each anion.

Anion	Migration Time, min		Peak Area	
	Mean	% RSD	Mean	% RSD
chloride	3.307	0.63	6.452	1.47
thiosulphate	3.557	0.34	6.673	1.73
sulphide	3.855	NA	NA	NA
sulphate	4.160	0.46	5.446	1.22
oxalate	4.657	0.22	5.317	0.91
sulphite	5.082	0.71	4.385	1.82
formate	5.960	0.89	5.775	1.56

% RSD = percentage relative standard deviation
NA = not applicable

Table 2.2. Linear regression results obtained from a plot of peak area versus concentration for a standard mixture of anions over the concentration range 1-50 mg/L.

Anion	Linear Regression Results		
	Slope	Intercept	Correlation Coefficient, R
chloride	6.517	0.0340	0.995
thiosulphate	5.758	0.625	0.994
sulphide	NA	NA	NA
sulphate	5.301	0.005	0.993
oxalate	4.907	0.367	0.996
sulphite	5.864	-1.033	0.993
formate	5.601	-0.0324	0.995

2.3.2 Analysis of Kraft Black Liquor

The feasibility of using cadmium (in the form of the acetate salt) to selectively remove sulphide from samples prior to analysis was tested on a sample of black liquor known to contain sulphide. Separate samples of black liquor were diluted 1:1000 with He-sparged water in the presence and absence of 10 mg/L of Cd^{2+}. The two black liquor samples and a standard mixture of anions excluding sulphide were then analysed. As indicated in Figure 2.4, the sample of liquor which received the Cd (upper trace) showed no peak for sulphide. The sample of liquor which did not receive any Cd shows a small peak for sulphide which is very similar in appearance to that observed with the standard solution (see Fig. 2.1). It is also evident from this figure that the migration times for the standard and samples are very similar despite the relatively high ionic strength and pH of the sample. This is due to the high ionic strength and buffering capacity of the electrolyte used in the separation, and is one of the attractive aspects of using CE with conductivity detection.

A few additional experiments were done to assess the impact of cadmium on the other anions present in the sample. This was done by comparing the concentration of the various anions in three standard solutions. One solution contained all anions, but no sulphide or cadmium; the second solution contained all anions including sulphide and cadmium (20 mg/L Cd^{2+}); and the third solution contained all anions, including cadmium, but no sulphide. The study revealed that 20% of the sulphite was oxidized to sulphate in the standard containing cadmium only. About 5% of the sulphite was oxidized to sulphate in the standard containing both cadmium and sulphide. These results suggest that cadmium is catalysing the oxidation of sulphite to sulphate and that the extent of the reaction may depend on the concentration of free cadmium in solution and possibly on the concentration of oxygen. Consequently, the use of cadmium to remove sulphide prior to sample analysis may also impact upon the reliability of the results obtained for sulphite and sulphate.

Subsequent to this work, many unsuccessful attempts were made to determine alkali and alkaline earth cations using established procedures. During our work we observed poorly resolved and tailing peaks for Na and Ca, and we also observed poor baseline stability. While looking for the cause of these problems, it was discovered that the ConCap and ConTip surfaces had become discoloured with a light brown deposit. A closer examination of both components using a microscope revealed that the deposit looked very much like rust and the same deposit could also be seen on the inner walls of the outlet end of the capillary. Figure 2.5 shows colour images of the surfaces of the ConCap and ConTip as recorded with a CCD attached to the light microscope. X-ray analysis of the surface deposits by scanning electron microscopy (SEM-EDS) revealed the presence of iron oxide, which confirmed the presence of rust on each component. It was later learned from the manufacturer that the detector cell block which houses the ConTip and ConCap components was constructed from 304 grade stainless steel. This grade of steel is not very resistant to corrosion, especially when in contact with acidic solutions.

The results obtained thus far suggest that the conductivity detector is not suitable for analysing sulphide-bearing samples. A more serious issue is the corrosion of the conductivity cell components, which could impact upon the reliable operation of the detector, regardless of the analytes being studied.

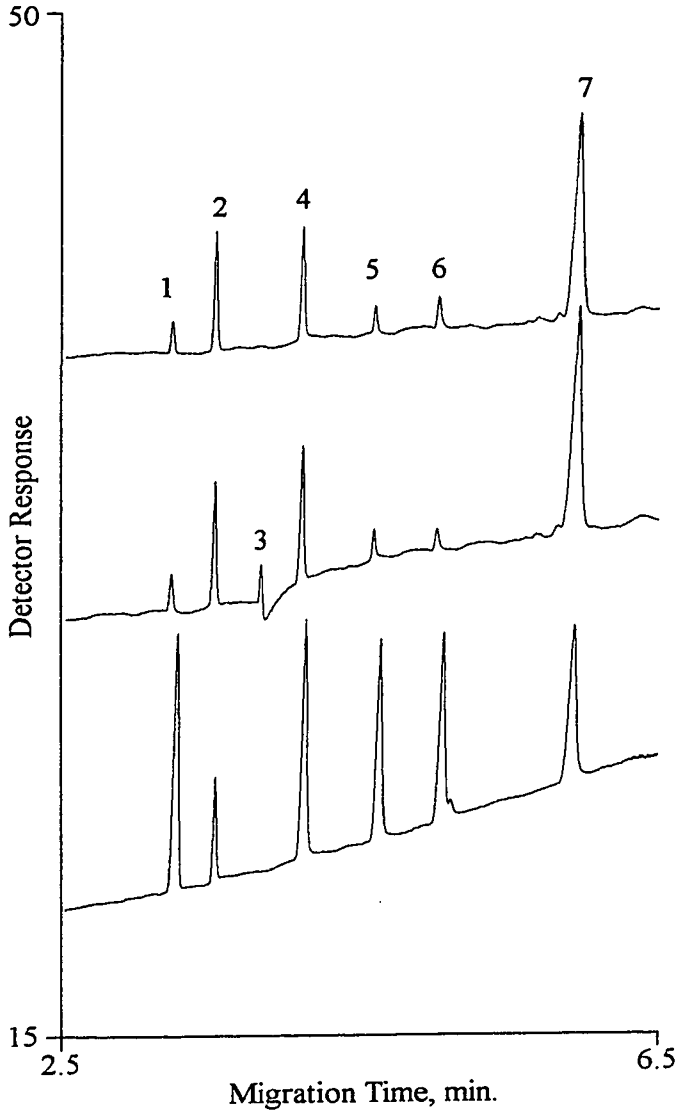

Figure 2.4. Separation of anions in a standard mixture (lower trace) and dilute black liquor diluted 1:1000 without Cd (middle trace) and with Cd (upper trace). The standard mixture contained 5 ppm each of chloride (1), thiosulphate (2), sulphate (4), oxalate (5), sulphite (6) and formate (7). Peak 3 in the center trace is sulphide. See Experimental for other analytical conditions.

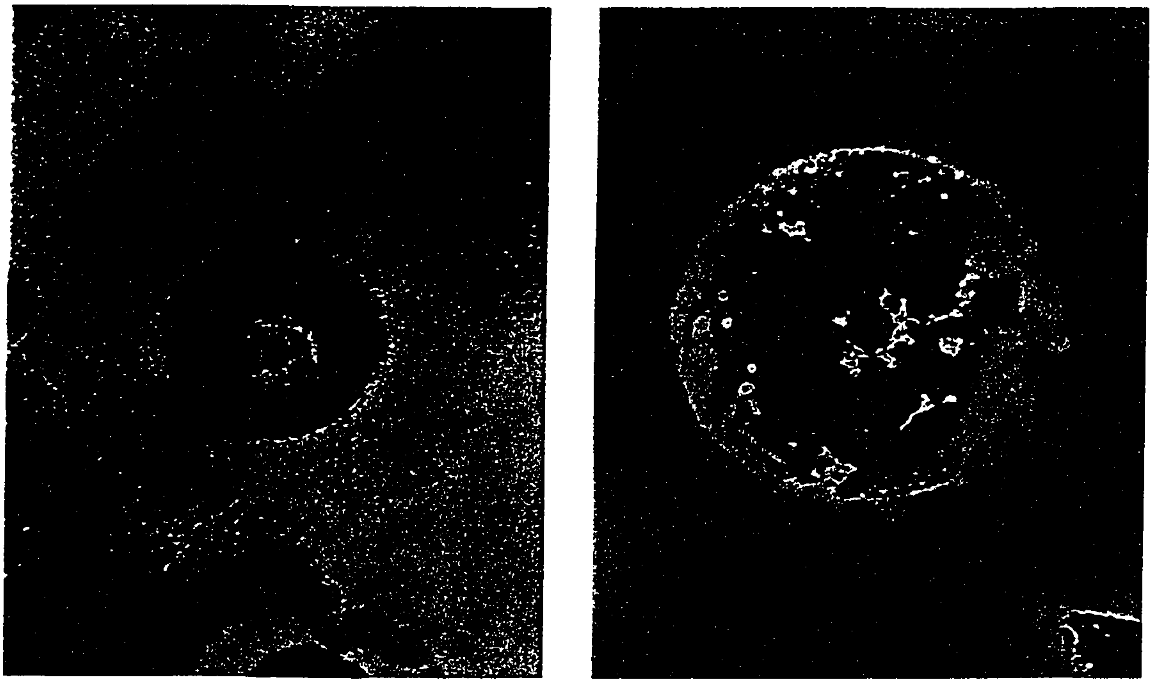

Figure 2.5. Photomicrographs of the surfaces of the outlet end of the ConTip sensor (left) and ConCap capillary (right), showing the presence of brown deposits. Magnification was 71x in each case.

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CHAPTER 3

ANALYSIS OF SULPHUR SPECIES IN KRAFT MILL PULPING LIQUORS BY CAPILLARY ELECTROPHORESIS USING INDIRECT UV-DETECTION

3.1 Introduction

The majority of the global production of unbleached and bleached chemical pulp is produced by the kraft process. Wood is the primary source of lignocellulosic material used in kraft pulping. The goal in kraft and other chemical pulping processes is to degrade and dissolve away the lignin present in the wood and leave behind most of the cellulose and hemicellulose in the form of intact fibres. The largely delignified fibres are then used as is to make unbleached pulp or they are bleached to produce high quality pulp and paper products. Because lignin is highly polymerized and linked with carbohydrates within wood, rather harsh conditions are necessary to rupture these bonds. In the kraft process, delignification is accomplished by heating (cooking) wood chips in a solution containing NaOH and Na_2S (known as white liquor), at temperatures of 170-180°C for 2-3 hours [1,2]. Increasingly, white liquor containing Na_2SS_n and/or anthraquinone is being used to improve the retention of hemicellulose and thus increase the yield of pulp from the process [3-6]. Industrial white liquor also contains variable but significant levels of $Na_2S_2O_3$, Na_2SO_3, Na_2SO_4, Na_2CO_3 and NaCl [7-9]. During the cook, hydroxide, sulphide and polysulphide are consumed. At the end of the cook, about 80% of the lignin, 50% of the hemicellulose and 10% of the cellulose originally present in the wood has been dissolved in the spent white liquor, and a large portion of the alkali (hydroxide), sulphide and polysulphide have been consumed through acid-base, hydrolysis, substitution and redox reactions with the wood components. At this point in the process, the spent white liquor is referred to as weak black liquor (WBL). Weak black liquor is a complex mixture containing hundreds of compounds, including low and high molecular weight lignin fragments, phenolic compounds, carbohydrates, organic acids and several inorganic species. The total content of dissolved solids present in WBL is 10-20% (w/w).

To ensure the economic viability of the kraft process, it is necessary to recover the carbon, sulphur and sodium present in the WBL. This is done by first concentrating the WBL in an evaporator followed by incineration of the resultant strong black liquor (SBL) in a furnace. During incineration, energy in the form of steam is generated from the combustion of the organic compounds and the important inorganic compounds present in the SBL are recovered as molten Na_2S and Na_2CO_3 (smelt). The smelt is dissolved in water to form green liquor (GL) which is then reacted with quick lime ($Ca(OH)_2$) to convert Na_2CO_3 into NaOH and thus regenerate the original white liquor (Na_2S + NaOH). As mentioned earlier, industrial WL contains appreciable levels of impurities (non essential inorganic ions) such as chloride, sulphate, thiosulphate and carbonate. The sources of the major anionic impurities, such as oxysulphur ions and carbonate, arise from inefficiencies in the recovery process, while chloride originates from the make up chemicals and the wood.

To minimize the degradation of cellulose and hemicellulose and maximize delignification, it is important that the quality of the white liquor used, as well as the temperature and duration of the digestion step be controlled to close tolerances. While the latter two parameters can be controlled quite accurately, monitoring and control of liquor quality is much more difficult because of the complexity of the various process liquors. The anions of critical importance in chemical recovery and to pulp quality, include: hydroxide, sulphide, polysulphide, carbonate, thiosulphate, sulphite, chloride. Over the years, many off-line gravimetric and/or titrimetric methods have been developed to measure the various anions in green, white and black liquors [10-16]. All of these methods are limited in their scope, and the ease and speed with which the anions can be determined. More modern instrumental methods utilizing ion chromatography [17-19] have been successfully applied to the analysis of anions in kraft liquors, but these methods are time consuming and require the use of several expensive columns which are susceptible to fouling after repeated exposure to black liquor. More recently, off-line and on-line flow injection analysis (FIA) [20-23], and on-line Fourier transform infrared (FT-IR) spectrometry-based methods have been developed [24,25], but they suffer from one or more of the limitations described above.

Capillary electrophoresis (CE) has emerged over the last decade as a powerful analytical technique for separating a wide variety of organic and inorganic solutes [26-30]. Capillary zone electrophoresis (CZE) is one of the most widely used forms of CE for separating low molecular weight inorganic and organic ions [31]. The most widely used approach for the analysis of anions involves the use of an electrolyte composed of sodium chromate and a long chain alkyl quaternary amine (cationic) surfactant with indirect UV-detection [32]. This approach has evolved and matured, and a number of validated methods have been published for determining several common inorganic and organic anions in simple matrices such as water samples. However, to date, no validated CE method has been published for the analysis of more complex samples, such as those encountered in the pulp and paper industry.

The main objective of the current work was to develop rapid off-line CE-based methods suitable for simultaneously separating and quantifying a broad range of inorganic species and organic acids present in kraft mill process liquors. It was felt that many of the limitations inherent in existing analytical techniques could be overcome by using a CZE-based method. At the outset of this work, only one paper by Salomon and Romano had been published on the analysis of anions in kraft mill effluents by CZE. Their approach utilized a chromate-based electrolyte system [33]. This work showed the potential of CZE to separate key anions in kraft process liquors, but it did not demonstrate that the approach was suitable for quantitative analysis. Subsequently, two additional publications by a group at the University of Innsbruck have appeared [34,35]. The authors 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; in fact, they noted that sulphide was very unstable in black liquor samples diluted for analysis.

In the current work, we describe a new method for determining the major anions in kraft white, green and black liquors. The method employs a simple electrolyte system which provides baseline resolution of the anions of interest. In addition, the cause of sulphide instability in dilute black liquor samples was found to be primarily due to an oxygen-mediated redox reaction between sulphide and quinones and/or quinone-like structures present in dissolved lignin. A simple and effective method was developed for stabilizing sulphide in the presence of quinones and in black liquor samples. The approach simply involves dilution of sample in an alkaline solution of glutathione, which is a biologically significant antioxidant. The new CZE method was validated and can be used to quantify the major anions in the various process liquors.

3.2 Experimental

3.2.1 Materials

3.2.1.1 Chemicals

Analytical grade sodium chromate tetrahydrate and sodium sulfide nonahydrate were obtained from Mallinckrodt (St. Louis, MO, USA). High purity sulphuric acid (Ultrex grade) was from J.T. Baker (Phillipsburg, NJ, USA), Tetradecyltrimethylammonium bromide (TTAB), sodium hydroxide, sodium sulphite, sodium sulphate, sodium thiosulphate, sodium chloride, sodium carbonate, sodium oxalate, sodium formate, sodium glycolate, lactic acid, sodium propionate, sodium butyrate, glutathione (GSH, reduced form), cysteine (CY), sodium mercaptoacetate (MAc), 1,4-benzoquinone (BQ), 2-hydroxymethyl-6-methoxy-1,4-benzoquinone (HMBQ), 2-hydroxy-1,4-naphthoquinone (HNQ), anthraquinone-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).

3.2.1.2 Apparatus

Studies were performed with a Crystal 310 CE instrument equipped with a model 4225 UV/Vis detector from Thermo Bioanalysis (Franklin, MA, USA). The Instrument control and data acquisition were conducted using Thermo Bioanalysis software (version 1.3

beta) and the 4880 data acquisition package (version 3.0). The data acquisition rate was set to 20 Hz. The polarity of the detector signal was reversed so as to obtain positive peaks. Bulk fused-silica capillary tubing (75 µm i.d x 363 µm o.d) was obtained from Polymicro Technologies (Phoenix, AZ, USA). Individual capillaries with a total length of 85 cm (Lt) and effective length to detector of 70 cm (Ld) were cut from the bulk tubing with the aid of a ceramic knife. A 5 mm wide detection window was created by burning off the polyimide coating with a butane lighter. A convenient way to control the width of the window is to place two pieces of aluminum foil about 5 mm apart near the point where the detection window is to be located, prior to burning the polyimide as described above. The window was then cleaned with a lens tissue wetted with acetone. Unless specified otherwise, separations were performed using the constant current mode, at ambient room temperature, with a negative polarity applied to the inlet end of the capillary. All samples were injected using pressure of 25 mBar for 12 seconds, which is equivalent to 34 nL of sample injected.

3.2.2 Methods

3.2.2.1 Electrolyte Preparation

The background electrolyte used for indirect UV detection was comprised of analytical grade sodium chromate tetrahydrate and teradecyltrimethylammonium 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 Milli-Q water. Prior to use, the electrolyte was degassed by sonication for 5 minutes and then filtered through a 0.5 µm syringe filter (Millex-LCR, Millipore) into 4 mL glass autosampler vials. The capillary outlet vial was filled with ca. 35 mL of unfiltered electrolyte.

Stock TTAOH solution was prepared by converting TTAB to the hydroxide-form as follows: Approximately 125 mL of a 20 mM TTAB in water was allowed to flow under gravity through a 60 mL polypropylene syringe containing ca. 40 mL of washed Dowex-1 resin (Nuclear grade, OH-form, 100 mesh, Sigma Chemical Co., St. Louis MO). The last 100 mL of eluate was collected and stored in a 125 mL polypropylene bottle (Nalgene) at room temperature. Prior to use, the Dowex-1 resin was washed with 50 mL of 1M NaOH and 150 mL of Milli-Q water.

3.2.2.2 **Capillary Cleaning Protocol**

Capillary cleaning was done according to the protocol described in Chapter 2.

3.2.2.3 **Standards and Solutions**

Standard stock solutions of the various anions and mixed standards were prepared as described in Chapter 2.

Stock GSH solutions (10 mg/mL) were prepared fresh daily by dissolving 500 mg of GSH and 2.5 mL of 2 M NaOH in 50 mL of He-sparged water. All solutions and samples were prepared and stored in polymethylpentene (PMP) flasks (Fisher Scientific).

3.2.2.4 **Preparation of Samples**

Samples of green, white and black liquors were obtained from several Canadian kraft mills and stored at 4 °C. With the exception of black liquor, all samples were diluted in He-sparged water, filtered through a 25 mm x 5 µm PTFE membrane syringe filter (Chromatography Sciences Company (CSC), St. Laurent, QC) and analysed immediately. Black liquor samples were prepared for analysis by first filtering ca. 5 mL of undiluted sample through a 5 µm PTFE filter (CSC) into a 5 mL polypropylene screw cap vial. To prevent the oxidation of sulphide during sample dilution, black liquor must be diluted in water containing GSH and processed as follows. To a 100 mL volumetric flask, was added 80 mL of He-sparged water and 10 mL of stock GSH solution, then 0.20 to 0.40 mL of filtered black liquor was delivered to the flask and the contents of the flask were then quickly diluted to volume with He-sparged water, briefly mixed and analysed immediately.

3.3 Results and Discussion

When research began in early 1996, the only publication on the analysis of anions in kraft liquors was that by Salomon and Romano [33]. The authors showed that the major anions in kraft liquors could be separated by CZE with indirect UV-detection using an electrolyte system based on that developed by Jones and Jandik [32]. The electrolyte was comprised of sodium chromate, sodium hydroxide, sulphuric acid, and an EOF modifier known as Nice-Pak OFM Anion-BT, which is commercially available from Waters Chromatography (Bedford, MA, USA) [31]. The active or primary ingredient in OFM-Anion-BT is the cationic surfactant TTAB, which is commercially available from many chemical suppliers. My initial work focused on evaluating their method for separating the major anions of interest using standard mixtures. In the course of the evaluation, a number of problems and/or deficiencies in their published method were identified, including: 1) the recommended detection wavelengths were found to be inappropriate for determining sulphide, 2) the electrolyte composition was found to be unsuitable for resolving oxalate and sulphide and 3) large variations were found in migration times between standards and samples as well as poor migration time reproducibility. As the evaluation progressed, it became clear that these problems significantly limited the reliability and utility of their method. Through a series of experiments, a number of effective solutions and strategies were developed to overcome these problems, as described in the following sections.

3.3.1 Evaluation of the Method of Salomon and Romano

3.3.1.1 Detection Wavelength and Electrolyte Considerations

The criteria for selecting a detection wavelength when using indirect photometric detection include: 1) the wavelength chosen should coincide or approximate the absorption maxima of the background electrolyte co-ion (chromate in this work) and 2) the analytes must be transparent at the selected wavelength. After examining the paper by Salomon and Romano, it was noticed that the wavelengths chosen by the authors were unsuitable for monitoring sulphide. As indicated in Figure 3.1, both sulphide and chromate absorb quite strongly at the two wavelengths used in their work (214 and 254 nm). From the same Figure it would appear that 275 nm is a more suitable detection wavelength because chromate has an absorption maxima ($\epsilon = 3.3 \times 10^3$ L cm^{-1} mol^{-1}) and sulphide as well as all other analytes are transparent at this wavelength. It is important to note that chromate possesses an additional, stronger absorption maxima ($\epsilon = 4.5 \times 10^3$ L cm^{-1} mol^{-1}), centered near 375 nm. In principle, it would be advantageous to use a detection wavelength of 375 nm, but it was found that the signal-to-noise (S/N) ratio at 275 nm was significantly better than that obtained at 375 nm.

Using a detection wavelength of 275 nm and the analytical conditions recommended by the authors, replicate analyses of a standard mixture of anions were performed. As illustrated in Figure 3.2, most anions were well resolved using these conditions, however, two key ions, namely sulphide and oxalate were found to comigrate. Interestingly, the authors did not report this problem in their paper. Because oxalate and sulphide are only found together in black liquor, it is not surprising that the authors did not observe comigration while analysing white and green liquors. Comigration may not have been observed during black liquor analysis due the absence of sulphide in the sample (as a result of oxidation of sulphide) or perhaps because the sulphide peak was attenuated as a result of the detection wavelengths used. However, it is surprising that comigration of oxalate and sulphide was not observed during the analysis of standards.

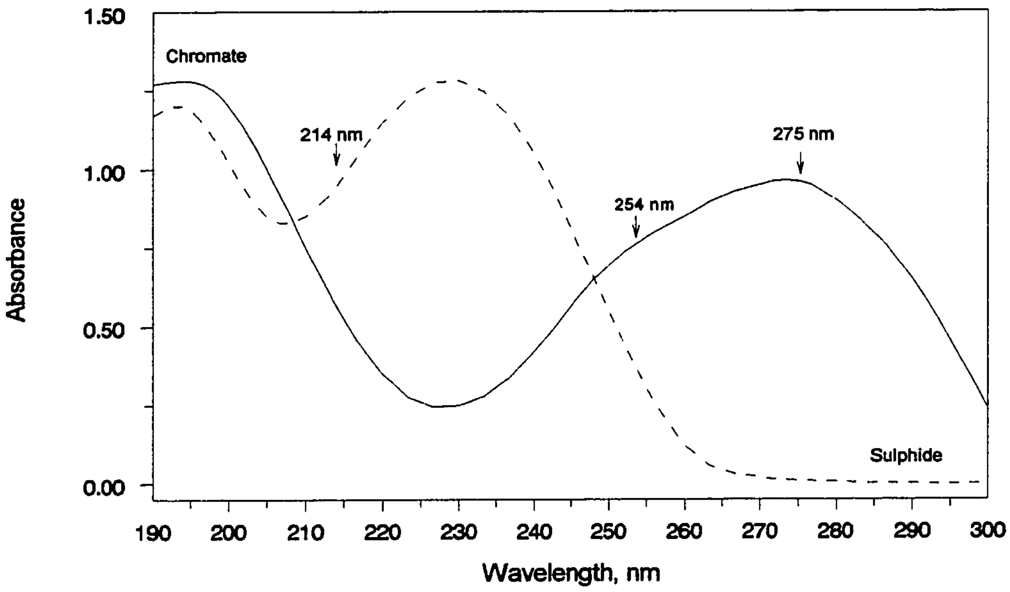


Figure 3.1. Absorption spectra of sodium chromate and sodium sulphide at pH 11, from Salomon and Romano [33].

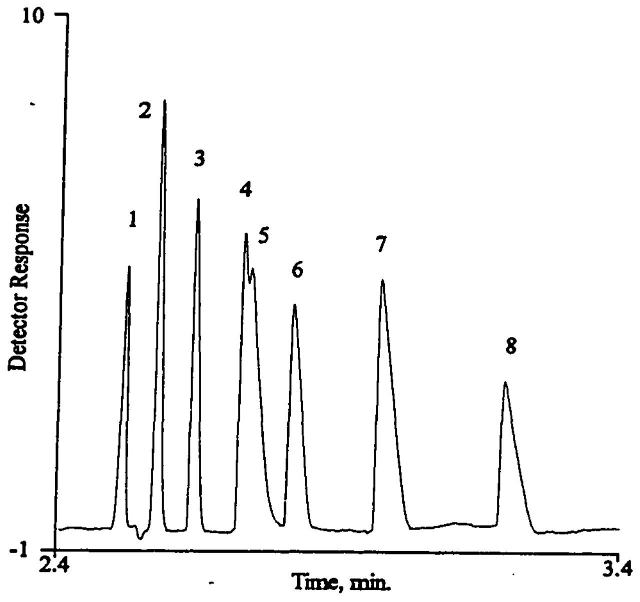


Figure 3.2. Separation of anions in a standard mixture. The electrolyte contained 5 mM chromate, sulphuric acid, 0.5 mM TTAB and NaOH (final pH 10.8). Peaks: Thiosulphate (1), chloride (2), sulphate (3), oxalate (4), sulphide (5), sulphite (6), carbonate (7), formate (8). The small negative peak between thiosulphate and chloride is due to bromide. All solutes (except bromide) were present at 10 mg/L. The separation was performed using constant voltage (-20 kV). See text and Experimental for other conditions.

3.3.1.2 Optimization of Electrolyte and Selection of Detection Wavelength

In an effort to improve the resolution of oxalate and sulphide, the following modifications were made to the electrolyte: 1) the chromate concentration was reduced to 4.5 mM from 5 mM, 2) the concentration of surfactant was reduced to 0.25 mM from 0.5 mM and 3) the hydroxide form of the EOF modifier (TTAOH) was used instead of the bromide form (TTAB). Reducing the chromate concentration results in an increase in the thickness of the electrical double layer on the inner surface of the capillary and thus an increase in the zeta potential. Decreasing the surfactant concentration results in a decrease in the pH of the electrolyte and a reduction in the EOF, which results in longer migration times for the analytes. The benefits gained from using TTAOH instead of TTAB include: 1) elimination of the bromide ion from the electrolyte, which eliminates the negative bromide peak found in the electropherogram between chloride and thiosulphate and 2) elimination of the need to add NaOH to the electrolyte because of the hydroxide contribution from the TTAOH. The latter modification greatly simplifies the preparation of the electrolyte.

As illustrated in Figure 3.3, baseline resolution of oxalate and sulphide was achieved using the modified electrolyte system described above. Also shown is the effect of detection wavelength on the intensity of the signals (peak areas) for the various analytes. As indicated, the peak for sulphide is severely attenuated at 254 nm for the reasons mentioned earlier. Although the largest peak areas were obtained at 375 nm, the most favourable S/N ratio was found at 275 nm. A summary of the peak areas obtained for a standard mixture of anions using the three detection wavelengths are presented in Table 3.1.

3.3.1.3 **Development of Strategies for Improving Migration Time Repeatability**

In CZE, electrolyte pH influences the electrophoretic mobilities of the analytes and the magnitude of the EOF, which in turn affects the selectivity of the separation and the reproducibility of the migration time. Inherent characteristics of chromate-based electrolytes used in inorganic anion separations are their low buffering capacity and relatively low ionic strength. 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.

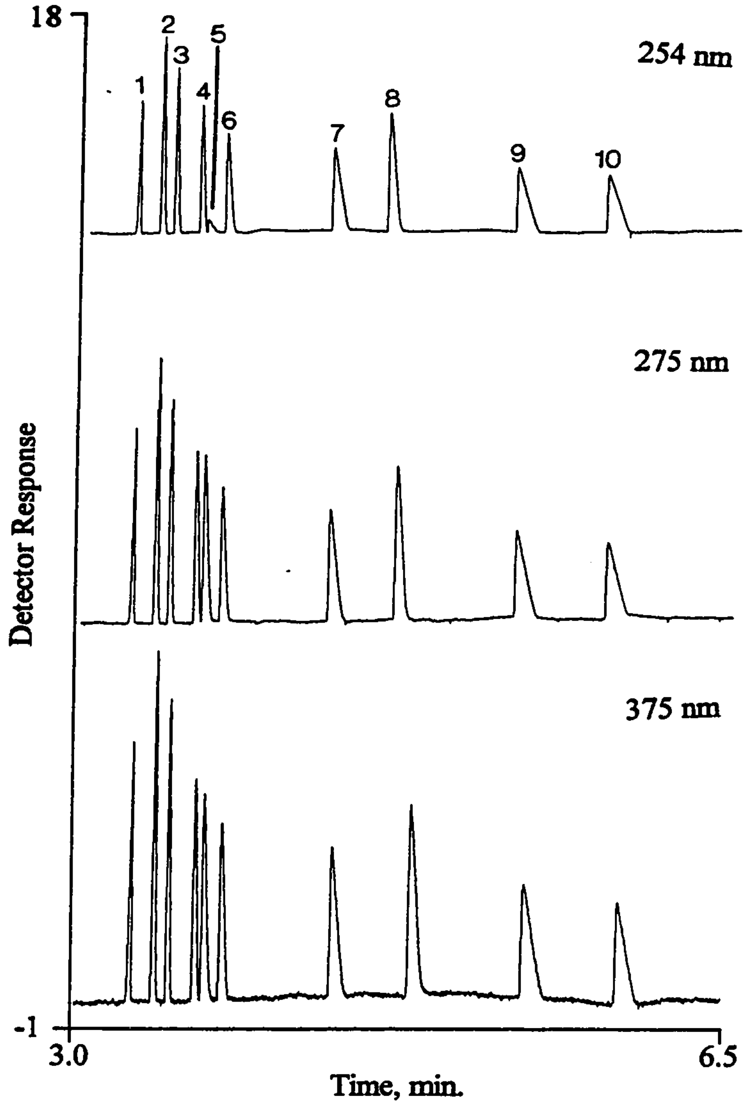


Figure 3.3. Separation of anions in a standard mixture, using the optimized conditions. Electrolyte comprised of 4.5 mM chromate, sulphuric acid and 0.25 mM TTAOH, ambient pH 10.2. Separations performed using constant current (-16 µA). Detection at 254, 275 and 375 nm. Peaks: Thiosulphate (1), chloride (2), sulphate (3), oxalate (4), sulphide (5), sulphite (6), formate (7), carbonate (8), acetate (9), propionate (10). All solutes present at 10 mg/L. See text and Experimental for other conditions.

Table 3.1. Effect of detection wavelength on signal intensity. Results obtained by replicate injections of a standard solution containing 10 mg/L of each anion at the specified detector wavelengths. See Experimental for other analytical conditions.

Anion	**Peak Area**			**Peak Area Ratios**	
	375 nm	**275 nm**	**254 nm**	**254/375**	**254/275**
thiosulphate	3.66	2.80	1.87	0.51	0.67
chloride	6.41	4.72	3.45	0.54	0.73
sulphate	5.92	4.29	3.10	0.52	0.72
oxalate	5.22	3.88	2.86	0.55	0.74
sulphide	**6.50**	**5.03**	**0.36**	**0.06**	**0.07**
sulphite	5.80	4.12	3.01	0.52	0.73
formate	6.95	5.42	4.03	0.58	0.74
carbonate	9.16	7.12	5.09	0.56	0.72
acetate	7.97	5.83	4.20	0.53	0.72
propionate	7.83	5.34	4.32	0.55	0.81

Electrolysis leads to an increase in the pH at the cathode (capillary inlet), where the OH^- ions are formed and a decrease in pH at the anode, where H^+ ions are formed [36]. Consequently, the conductivity of both the inlet and outlet electrolytes will increase and thus their resistance (R) will decrease over time. If separations are performed using a constant voltage (V), then the current (I) flowing through the electrolyte must increase with time, according to Ohm's Law (V=IR). However, if separations are performed using a constant current, then the voltage across the capillary will decrease over time. It is well known that the velocity of the EOF (v_{EOF}) is linearly related to the field strength (E=V/L) and the current , according to the relationships shown in equations 8 and 9 [37].

$$v_{EOF} = -\frac{\varepsilon\varepsilon_0\zeta}{\eta}E = \mu_{EOF}\frac{V}{L} \tag{8}$$

$$v_{EOF} = -\frac{\varepsilon\varepsilon_0\zeta}{\eta}\frac{IR}{L} = -\frac{\varepsilon\varepsilon_0\zeta}{\eta}\frac{I}{Ak} = \mu_{EOF}\frac{I}{Ak} \tag{9}$$

Where ϵ is the dielectric constant of the solvent, ϵ_0 is the permittivity of the vacuum, ζ is the zeta potential, η is the viscosity of the medium, L is the length of the capillary, A is the cross-sectional area of the capillary and k is the conductivity of the solution. Since anion separations are conducted under coelectroosmotic flow conditions (EOF and anion migration are in the same direction), it follows that an increase in EOF will result in a decrease in analyte migration time. Consequently, performing separations under constant voltage conditions, without replenishment of the electrolyte between runs, would be expected to yield less reproducible migration times than those obtained under constant current conditions.

A number of workers have shown that the velocity of an analyte is linearly related to the separation current, even at high values of I typically used in CZE applications [38, and references therein]. If separations are performed under constant voltage conditions then the velocity of the analyte will increase and thus the analyte migration time will decrease as the electrolyte becomes hydrolysed ("depleted"). However, if separations are performed in the constant current mode, both the voltage and resistance will decrease over time as the electrolyte becomes depleted and the migration time of the analyte should remain relatively constant. The expected consequence of performing separations using constant current instead of constant voltage is a significant improvement in the repeatability of analyte migration times.

Recently, Jones et al. received a patent for a method of performing CZE with improved migration time reproducibility [39]. Their approach involves the use of a complex combination of constant current, constant voltage and constant power during the course of the analysis to compensate for changes in ionic strength and pH within and between samples. They also showed that migration times are more reproducible within and between samples when constant current as opposed to constant voltage was used. A more recent evaluation of constant current versus constant voltage was reported by Kurosu et al. [40]. The authors showed that migration time reproducibility within a sample was up to 6 times better using the constant current mode of operation. Similar benefits in terms of migration time reproducibility within and between samples were found in this work, when separations were performed using the constant current mode.

Another potential contributor to poor migration time reproducibility may arise from deposition or adsorption of dissolved substances such as lignin and polysaccharides present in the sample onto the inner surface of the capillary. The presence of these substances on the inner surface of the capillary alter the zeta potential and thus the EOF. If these substances are not removed after each run, then migration time will vary considerably from run-to-run. To address the issue of capillary column contamination which is particularly serious for the analysis of samples such as black liquor, a column cleaning procedure utilizing 0.5 M NaOH and water rinses at the end of each run was implemented. This effectively removes organic material (such as lignin) from the inner surface of the capillary. Using this approach, a very reproducible capillary surface chemistry and therefore EOF is obtained from run-to-run. As indicated in Table 3.2, migration time and peak area repeatability was excellent for all solutes using the constant current mode of operation in combination with the column cleaning protocol described above.

Table 3.2. Repeatability of migration time and peak area for a standard mixture of anions using the revised conditions. Each anion present at 5 mg/L.

Anion	Migration Time (% RSD, n=6)	Peak Area (% RSD, n=6)
thiosulphate	0.1	1.1
chloride	0.7	1.4
sulphate	0.7	0.8
oxalate	0.8	1.5
sulphide	0.1	2.0
sulphite	0.1	1.4
formate	0.4	1.8
carbonate	1.8	2.0
hydroxide	0.1	0.2
acetate	1.4	1.5
propionate	1.6	0.5

3.3.1.4 **Linearity of Detector Response**

A plot of peak area versus anion concentration was made for a series of mixed standards covering the range of 0.5 to 50 mg/L to determine the linearity of the detector response. As indicated in Table 3.3, the response for each ion was linear over the specified concentration range, with correlation coefficients ≥ 0.9997 for each ion.

Table 3.3. Linear regression results obtained from a plot of peak area versus concentration for standard solutions covering the concentration range 1-50 mg/L (1-50 mM for hydroxide).

Anion	Slope	Intercept	Correlation Coefficient (R)
thiosulphate	0.276	0.087	0.9999
chloride	0.499	0.024	0.9999
sulphate	0.414	0.053	0.9997
oxalate	0.395	0.002	0.9999
sulphide	0.588	-0.20	0.9998
sulphite	0.506	-0.080	0.9999
formate	0.542	0.038	0.9999
carbonate	0.646	0.959	0.9999
hydroxide	7.494	-0.22	0.9999
acetate	0.564	0.094	0.9999
propionate	0.582	-0.14	0.9999

3.3.1.5 Repeatability of Migration Time and Peak Area for Liquor Samples

Replicate analyses of samples of white (WL), green (GL) and black liquor (BL) were performed to assess the repeatability of the migration times and peak areas for the various anions. Each sample was diluted in He-sparged water and repeatedly analysed over the course of an hour. As shown in Figure 3.4, very good separation of the analytes was obtained using the optimized electrolyte. As indicated in Table 3.4, excellent migration time repeatability was also obtained for each ion in all samples examined. In general, peak area repeatability was quite good for most ions in each of the liquors studied. However, poor repeatability was found for sulphide, thiosulphate, and sulphite (% RSDs: 32, 9 and 13%, respectively) in the black liquor sample. After reviewing the data from the black liquor analyses, it was found that the peak area for sulphide had decreased, while those for thiosulphate and sulphite had increased throughout the analyses.

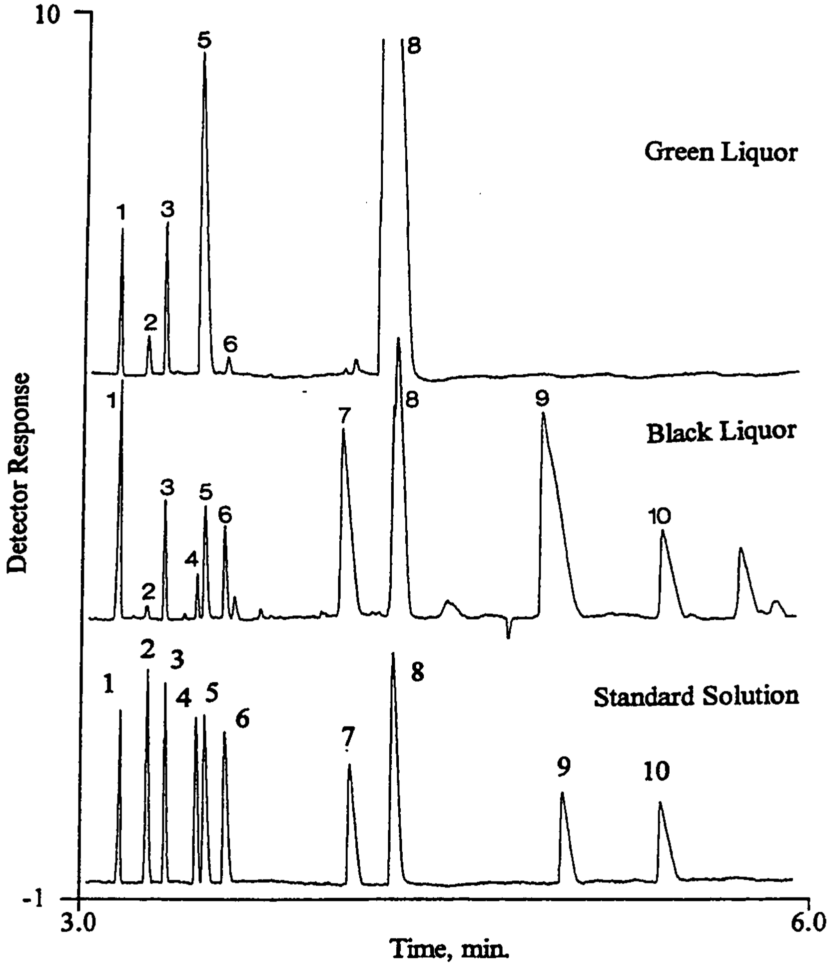


Figure 3.4. Separation of anions in green liquor (upper trace), black liquor (middle trace) and a standard mixture (lower trace). Electrolyte comprised of 4.5 mM chromate, sulphuric acid and 0.25 mM TTAOH, ambient pH 10.2. Separations performed using constant current (-16 μA). Detection at 275 nm. Peaks: Thiosulphate (1), chloride (2), sulphate (3), oxalate (4), sulphide (5), sulphite (6), formate (7), carbonate (8), acetate (9), propionate (10). All solutes present at 10 mg/L. See text and Experimental for other conditions.

Table 3.4. Repeatability of migration time and peak area obtained from replicate analyses of samples of white, green and black liquor.

Anion	Migration Time (% RSD, n=4)			Peak Area (% RSD, n=4)		
	WL	GL	BL	WL	GL	BL
thiosulphate	0.1	0.2	0.1	**3.0**	**1.2**	**8.9**
chloride	0.1	0.2	0.1	3.5	3.6	3.0
sulphate	0.1	0.2	0.1	1.5	1.1	1.8
oxalate	-	-	0.1	-	-	1.7
sulphide	0.1	0.2	0.1	**3.1**	**1.4**	**32.2**
sulphite	0.1	0.2	0.1	**3.6**	**4.0**	**12.9**
formate	-	-	0.1	-	-	1.1
carbonate	0.9	0.4	0.8	2.1	0.8	0.9

In a separate experiment, the same sample of black liquor was diluted in He-sparged water and the stability of the sulphur species was followed over the course of an hour. As illustrated in Figure 3.5, the sulphide peak area decreased to about 40 % of its initial value after 15 minutes and to about 5% after 65 minutes. Concurrently, the thiosulphate and sulphite peaks increased and then levelled off as the sulphide neared zero. The sulphate peak area remained constant over the same period.

As indicated in reactions 1-3, the chemistry of sulphide in aqueous systems is quite complex. In the presence oxygen, a number of reactions are known to occur [41,42]. As shown in Figure 3.5, the major sulphur species produced from the oxidation of sulphide include thiosulphate, sulphite, sulphate and polysulphide. If the oxidation of sulphide by oxygen was the sole mechanism by which sulphide is degraded in black liquor, then sulphide

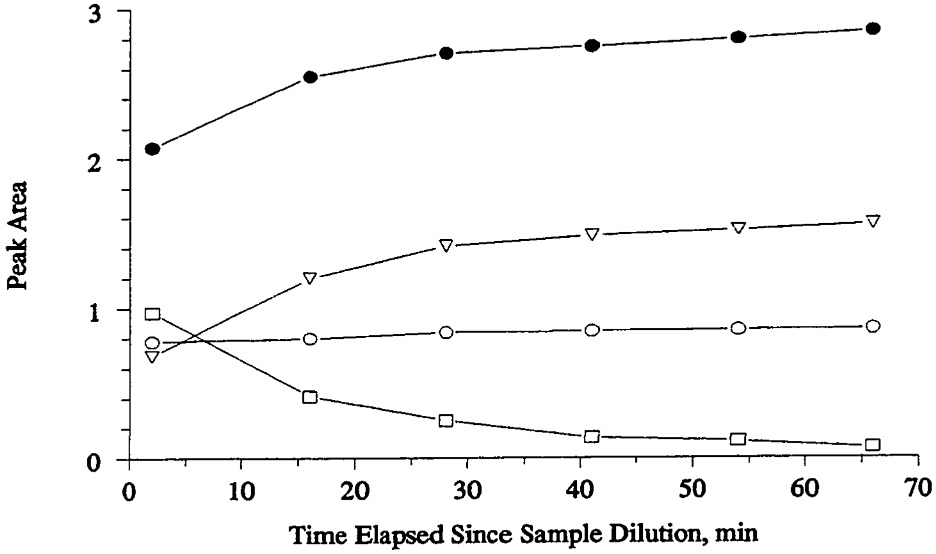


Figure 3.5. Effect of storage time on the stability of sulphide (□), sulphite (▽), thiosulphate (•) and sulphate (○) in dilute black liquor. Sample was diluted 1:500 in He-sparged water.

$$2HS^- + 2O_2 \rightleftharpoons S_2O_3^{2-} + H_2O \qquad (1)$$

$$2HS^- + 3O_2 \rightleftharpoons 2SO_3^{2-} + 2H^+ \qquad (2)$$

$$2SO_3^{2-} + O_2 \rightleftharpoons 2SO_4^{2-} \qquad (3)$$

Moreover, polysulphide (S_nS^{2-}, where $4 \geq n \geq 1$) is also produced, as shown in reaction 4.

$$(2n+2)HS^- + nO_2 \rightleftharpoons 2S_nS^{2-} + 2(n-1)OH^- + 2H_2O \qquad (4)$$

should have been equally unstable in the white and green liquors. However, as indicated in Table 3.4, this was not observed. The major difference between black liquor and the other two liquor samples is that black liquor contains a broad range of organic substances, including dissolved lignin and a range of lignin degradation products (aryl and alkyl phenolic compounds). The instability of sulphide in black liquor appears, therefore, to be related to the presence of the dissolved organic material. This phenomena has been reported recently by others [34,35]. The authors speculated that quinones may play a role in the oxidation of sulphide, but no proof was offered to support their hypothesis.

3.3.1.6 **Stability of Sulphide in the Presence of Model Quinones**

In the present work, it was also suspected that quinones may be participating in the oxidation of sulphide. A series of experiments were performed to test this hypothesis. Standard 1000 mg/L solutions of the quinones listed in Table 3.5 were prepared in deionized water and used immediately to prepare the solutions described below. Suitable aliquots of standard sulphide (S^{2-}) and quinone stock solutions were transferred to a volumetric flask and diluted to volume to give a 10 mg/L solution of each reagent. These sulphide/quinone solutions were then analysed immediately and at regular time intervals thereafter by CZE. The study revealed that sulphide was stable in the presence of AQDSA, AQCA and HNQ, but reacted with HMBQ to form thiosulphate exclusively, and with BQ to form primarily thiosulphate and sulphite with a small amount of sulphate, as illustrated in Figure 3.6. The initial rate of the reaction between BQ and sulphide is very fast, with approximately 75% of the sulphide being degraded within the first 2 minutes, followed by a nearly linear decrease over the next 48 minutes to about 5% of the original value.

Table 3.5. List of model compounds used in the quinone-sulphide stability study.

Compound	Abbreviation
Anthraquinone-1,5-disulphonic acid	(AQDSA)
Anthraquinone-2-carboxylic acid	(AQCA)
2-Hydroxy-1,4-naphthoquinone	(HNQ)
1,4-Benzoquinone	(BQ)
2-Hydroxymethyl-6-methoxy-1,4-benzoquinone	(HMBQ)

Thiosulphate levels increased rapidly between 2 and 20 minutes and then more slowly, and nearly linearly between 20 and 48 minutes. Sulphite increased over the first 35 minutes then began to decrease. A small, but constant level of sulphate was found between 2 and 50 minutes. The study revealed that the oxidation of sulphide in black liquor and in the presence of quinones results in the formation of similar types and relative amounts of the oxysulphur anions thiosulphate, sulphite and sulphate. The results also showed that not all quinones participate in the oxidation of sulphide.

To our knowledge, this is the first study to clearly demonstrate that quinones are capable of oxidizing sulphide to thiosulphate and sulphite. Moreover, this work illustrates the utility and power of CZE to rapidly monitor and quantify a broad range of species of interest with little or no sample preparation.

3.3.1.7 Development of a Strategy for Stabilizing Sulphide

After identifying quinones as being largely responsible for the oxidation of sulphide in synthetic samples, the focus turned to attempting to develop a simple and effective method for stabilizing sulphide in the presence of BQ and in dilute black liquor samples.

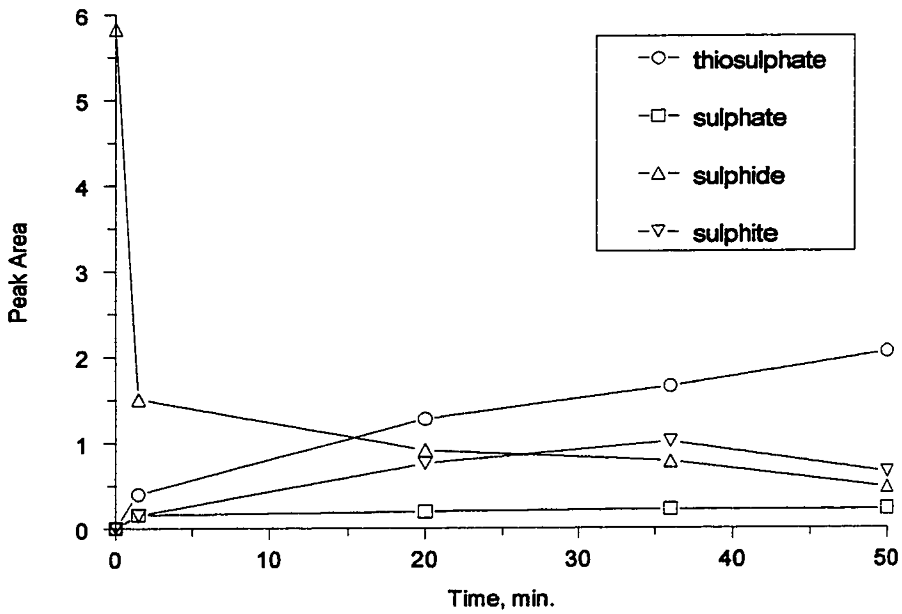


Figure 3.6. Stability of sulphide in the presence of 1,4-Benzoquinone. See text and Experimental for other conditions.

It was thought that quinones probably oxidize sulphide via a free-radical-based redox mechanism, and that it may be possible to halt this redox cycle and thereby stabilize sulphide using a free radical scavenger. Consequently, the initial part of this work focused on assessing the efficacy of selected compounds known to have radical scavenging ability.

Included among the many types of compounds used for this purpose are the thiols (RSH). Among the thiols, the tripeptide glutathione (γ-L-glutamyl-L-cysteinylglycine, GSH, reduced form) is one of the most important and effective biological free radical scavengers. Glutathione is present at millimolar concentrations in most cells of the body and plays an important role in maintaining the redox state of a wide variety of intercellular molecules, and in protecting cells during periods of oxidative stress [43]. In this work, GSH, cysteine (CY) and mercaptoacetate (MAc) were evaluated for their ability to stabilize sulphide in the presence of BQ and in dilute black liquor. Cysteine was included in the study because it is the amino acid in GSH that contains the sulphydryl (-SH) group, which is thought to be responsible for the efficacy of GSH. Mercaptoacetate also contains a sulphydryl group and is structurally similar to cysteine.

3.3.1.8 **Effectiveness of Thiols in Stabilizing Sulphide in the Presence of BQ**

The first step in the evaluation was to determine the migration times of the thiols, since comigration with the anions of interest would preclude their use in liquor samples. Analysis of the three thiols by CZE showed that GSH had the lowest mobility (longest migration time), eluting near acetate, while CY had a higher mobility than GSH (eluting after formate), and MAc had the highest mobility (nearly comigrating with carbonate). The results indicated that GSH was well resolved from the anions of interest, but MAc may interfere in the analysis of carbonate and possibly sulphite, and that CY may interfere with formate.

3.3.1.8.1 **Effect of GSH on the Stability of Sulphide in the Presence of BQ**

The effectiveness of GSH in stabilizing sulphide in the presence of BQ was studied by preparing several solutions containing constant concentrations of sulphide and BQ (10 mg/L each), and varying concentrations of GSH (0.1, 0.5 and 1.0 mg/L). To avoid loss of S^{2-} as H_2S, a small amount of NaOH was added to maintain an alkaline pH during the experiment (initial [NaOH] ca.0.5 mM). It should be noted that GSH has four ionizable functional groups (two carboxyl, one amine and one sulphydryl, pKa values: 2.12, 3.53, 8.66, 9.12). The solutions were prepared by combining the reagents in the following order: NaOH, GSH, BQ and sulphide and then analysed without delay and at regular intervals thereafter for up to one hour. The experiment showed that a GSH concentration of 1 mg/L stabilized sulphide for at least one hour in the presence of the chosen concentration of BQ. Lower levels of GSH were effective for shorter periods of time.

3.3.1.8.2 **Possible Mode of Action of GSH in Sulphide/BQ Solutions**

Like all quinones, BQ contains the chromatophoric quinoid group, which is largely responsible for the chemistry of the compound. As indicated in Figure 3.7 [44], BQ can be a one- or two electron acceptor (reactions 5 and 6, respectively) and thus its reduction can proceed by a one- or two electron transfer. In reaction 5, BQ is reduced to the semiquinone radical anion, while in reaction 6 it is reduced to hydroquinone (p-benzohydroquinone). As illustrated in reactions 7-9, semiquinone can be produced from the reaction of hydroquinone with oxygen and superoxide radical anion ($O_2^{\bullet-}$), and from the reaction of BQ with $O_2^{\bullet-}$. Reactive oxygen species such as H_2O_2 and $O_2^{\bullet-}$ are also produced in these reactions.

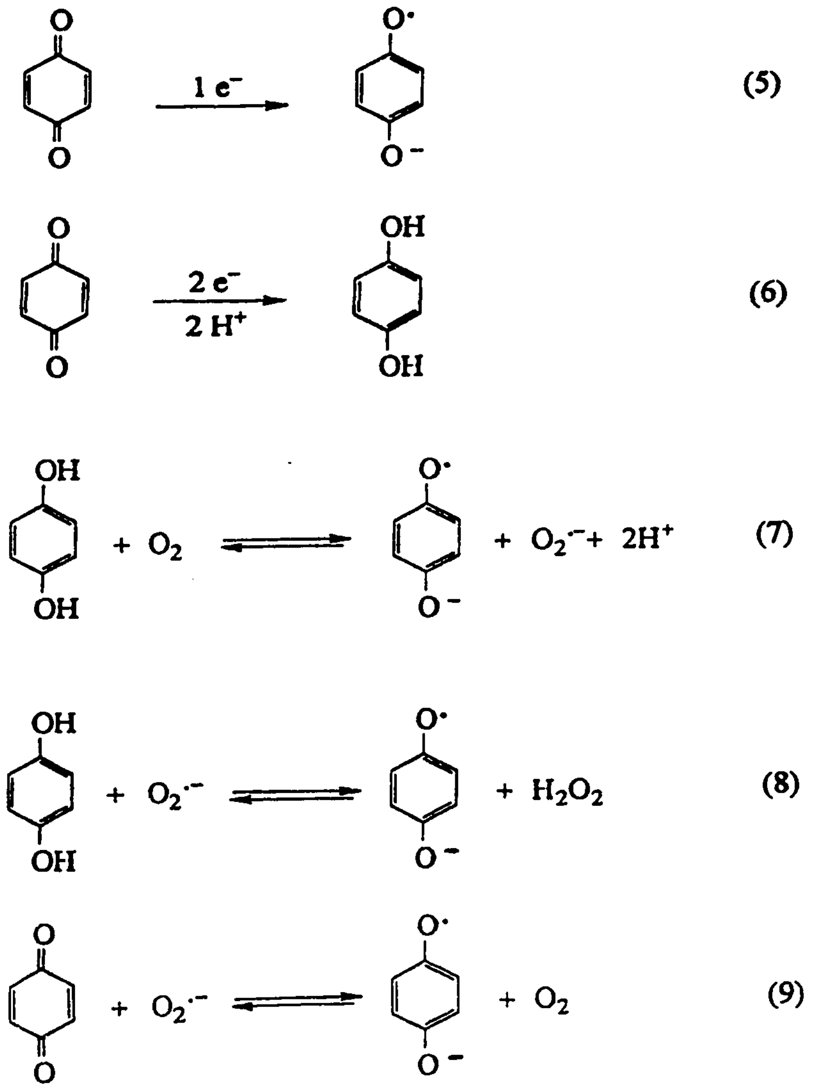


Figure 3.7. Important redox reactions of 1,4-benzoquinone (BQ) [44].

Additionally, BQ can react with $O_2^{\bullet -}$ to form the semiquinone radical anion and oxygen, as shown in reaction 9. It is evident from the discussion above, that when quinone radicals are produced, a number of equally reactive oxygen species are also generated, which together are capable of participating in a variety of redox reactions with a number of substrates.

It is recognized that BQ can also undergo nucleophilic substitution (1,4-reductive addition of the Michael type) by thiols such as GSH to produce a hydroquinonethioether adduct [44] and oxidised glutathione (GSSG). In addition, it has also been shown that the BQ-thioether adducts can exist as radical anions capable of participating in further redox reactions. It appears that most if not all of studies conducted to date on BQ/GSH systems have been done under acidic or neutral pH conditions. The reaction mechanisms and products generated in such systems may be different from those generated under the alkaline conditions used in this work. For example, BQ may be extensively polymerised under alkaline conditions [45,46], and thus may exhibit a range of redox reactivity.

The evidence from this work suggests that oxygen, quinones and sulphide may participate in a redox cycle in which sulphide is oxidized primarily to thiosulphate and sulphite, as illustrated in Figure 3.8 (A). As indicated the cycle begins with the reaction of oxygen with BQ radical anion to form oxidized quinone and superoxide radical anion. Oxidized quinone can then react with the sulphide (an electron-rich species) to form the oxysulphur species mentioned earlier. If oxygen is present, then the redox cycle can start once again and continue until the oxygen and/or the substrate (sulphide) is consumed.

However, the redox cycle can be broken by scavenging the free radicals as they are produced. As indicated in Figure 3.8 (B), one way in which the redox cycle may be broken is through the reaction of GSH with quinone radical anion to produce oxidized GSH (GSSG) and hydroquinone. Another way in which GSH can be beneficial is to react with superoxide radical anion and thus prevent the radical from reacting with hydroquinone to produce peroxide (reaction 8), which if formed, could oxidize sulphide to thiosulphate and sulphite. The maximum benefits from GSH should be realized by maintaining a high concentration of GSH and by minimizing the dissolved oxygen concentration in the sample.

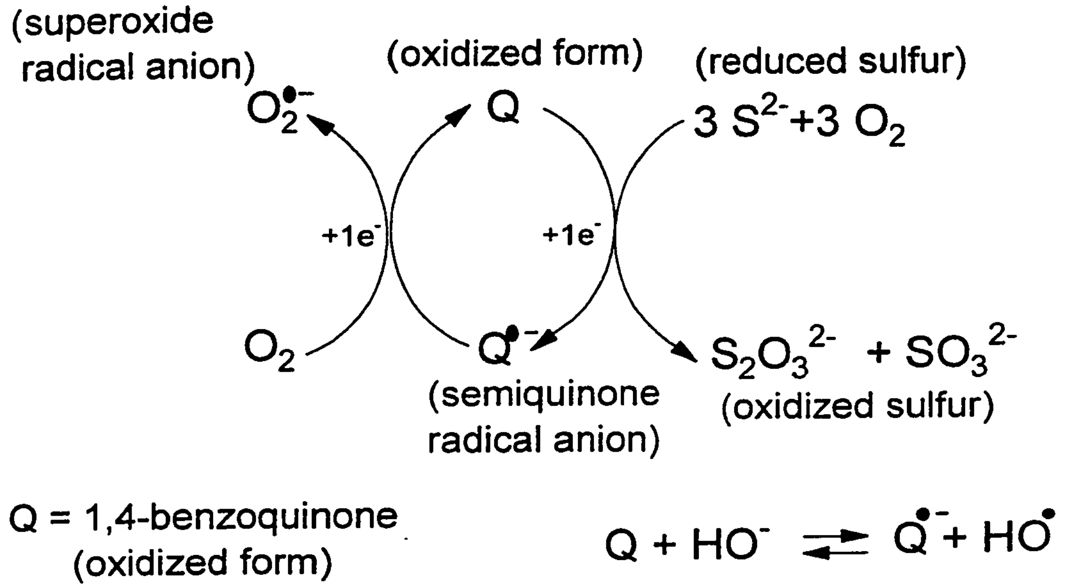
3.3.1.8.3 **Effect of CY on the Stability of Sulphide in the Presence of BQ**

The effectiveness of CY in stabilizing sulphide in the presence of BQ was assessed by preparing solutions containing the same levels of sulphide, NaOH, CY, BQ and sulphide as described above for GSH. Sulphide level in the various solutions were monitored as described above. The findings in this experiment parallelled those found with GSH. Sulphide was completely stabilized in the presence of BQ for up to an hour when CY was present at 1 mg/L. The results indicate that the cysteine is just as effective as GSH is stabilizing sulphide.

3.3.1.8.4 **Effect of MAc on the Stability of Sulphide in the presence of BQ**

The effectiveness of MAc in stabilizing sulphide in the presence of BQ was assessed by preparing a solution containing the same levels of sulphide, NaOH, BQ, MAc and sulphide as described earlier. However, only one level of MAc (1 mg/L) was used. Sulphide levels were monitored as described earlier. The results showed that MAc was ineffective in stabilizing sulphide. This also illustrates how a small difference in structure can result in a significant change in the efficacy of the thiol as a free radical scavenger.

A



B

$$2\ GSH + 2\ Q^{\bullet -} \longrightarrow GSSG + 2\ HQ$$

GSH = reduced glutathione
GSSG = oxidized glutathione

Figure 3.8. Possible mechanism for the oxidation of sulphide in the presence of BQ (A) and GSH as a free radical scavenger (B).

3.3.1.8.5 Effect of GSH and Oxygen on the Stability of Sulphide and Oxysulphur Anions in Dilute Black Liquor

As described earlier, it was discovered that GSH effectively stabilizes sulphide in the presence of BQ. However, it was not known whether this approach could be used successfully to stabilize sulphide in black liquor, which is inherently much more complex than the model system outlined above. The efficacy of GSH and the impact of dissolved oxygen on the stability of sulphide in black liquor was assessed by monitoring the sulphide levels in samples prepared in unsparged water, in He-sparged water and in He-sparged water containing 1 mg/mL of GSH. The sulphide and oxysulphur anion levels were monitored immediately after sample dilution and for up to one hour thereafter.

As indicated in Figure 3.9 (A), sulphide was stable for up to one hour in black liquor prepared in unsparged water containing 1 mg/mL GSH. In contrast, sulphide was less stable in the same sample prepared in He-sparged water and very much less stable in the sample prepared in unsparged water. In the latter sample, about 40% of the sulphide was decomposed during the first 1-2 minutes after sample dilution. This rapid drop in sulphide would not be detectable using other techniques currently in use, and thus the magnitude of the error in the sulphide result would not be apparent to the analyst.

As shown in Figure 3.9 (B), thiosulphate levels remained constant in the sample prepared in He-sparged water containing 1 mg/mL GSH. As expected, thiosulphate was less stable in the sample prepared in He-sparged water and least stable in the sample prepared in unsparged water.

The stability of sulphite and sulphate in the various black liquor samples are shown in Figures 3.10 (A) and (B), respectively. As expected, sulphite was most stable in the sample prepared in He-sparged water with GSH present and least stable in the sample prepared in unsparged water. While sulphide and thiosulphate were found to be completely stable in samples prepared in He-sparged water, interestingly, the same behaviour was not observed for sulphite. As indicated, sulphite was formed very rapidly in the sample prepared in unsparged water and much more slowly in the sample prepared in He-sparged water. The greatest stability was obtained for the sample prepared in He-sparged water with GSH present. However, even in this sample, sulphite increased nearly linearly from about 80 mg/L to about 500 mg/L over the course of an hour. These results strongly suggests that sulphite is not produced by a mechanism involving the oxidation of sulphide by quinones, rather, it implies that sulphite may be produced by the oxidation of another labile form of sulphur present in the sample. One such form of sulphur may be polysulphide (S_nS^{2-}). It is known that polysulphide can disproportionate and precipitate during sample dilution to yield elemental sulphur (S^0). The precipitated sulphur can then produce sulphite according to the following reaction [47].

$$3\,S^0 + 3\,H_2O \rightleftharpoons SO_3^{2-} + 2HS^- + 4H^+ \qquad (10)$$

Evidence for the existence of polysulphide in dilute black liquor will be discussed later. As illustrated in Figure 3.9 (B), sulphate was least stable in samples prepared in unsparged water and was most stable in samples prepared in He-sparged water with GSH present. Most of the increase in the sulphate level within a sample is due to the oxidation of sulphite, and thus

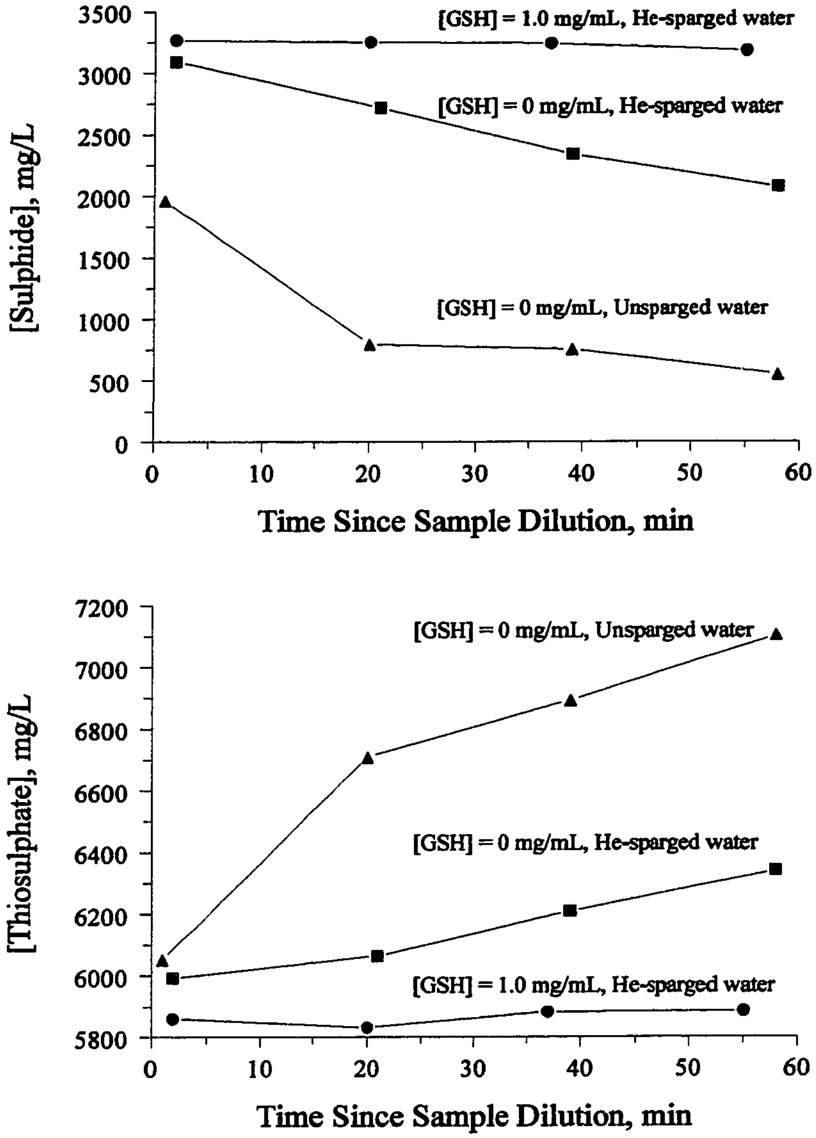


Figure 3.9. Effect of glutathione and solvent selection on the stability of sulphide (A) and thiosulphate (B) in dilute (1:250) black liquor. See text and Experimental section for other conditions.

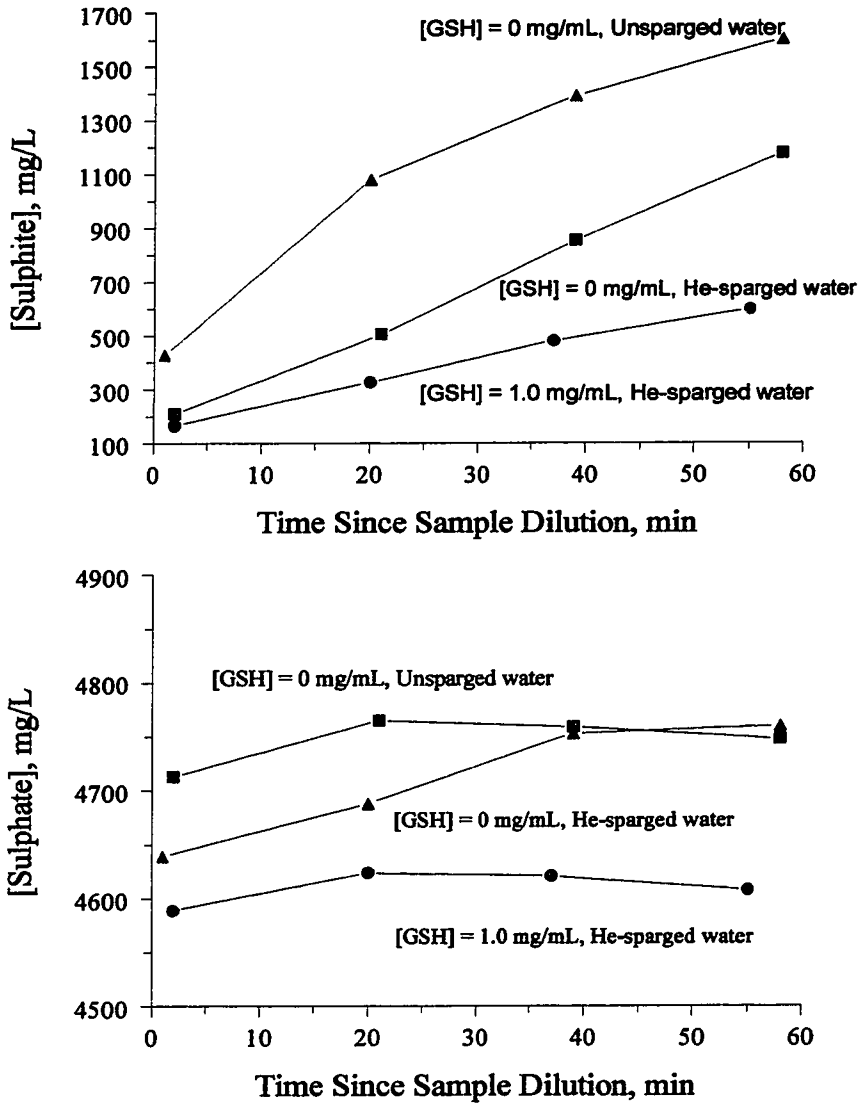


Figure 3.10. Effect of glutathione and solvent selection on the stability of sulphite (A) and sulphate (B) in dilute (1:250) black liquor. See text and Experimental section for other conditions.

the highest levels of sulphate should be found in a sample which contains high levels of sulphite and dissolved oxygen. The sulphate results obtained in this experiment are consistent with this hypothesis.

Results from the analysis of sulphide in dilute black liquor prepared in unsparged water and in the absence of GSH were similar to those obtained with the sulphide/BQ model system described earlier. In both cases, sulphide was rapidly degraded to thiosulphate, sulphite and sulphate. In addition, it was found that sulphide could be stabilized in dilute liquor and in the presence of BQ when samples were prepared in degassed water with GSH. The overall conclusions from the study are: 1) The oxidation of sulphide in black liquor is catalysed by quinones in the presence of dissolved oxygen, 2) The degradation of sulphide can be halted by preparing samples in degassed water containing sufficient GSH and 3) Quantitative analysis of sulphide and oxysulphur anions can only be done if black liquor samples are prepared as described above.

3.3.1.8.6 **Problems Encountered in the Analysis of Samples Containing Polysulphide**

In the course of analysing an aged white liquor sample, it was found that the thiosulphate peak exhibited significant tailing and a new peak between thiosulphate and chloride had appeared. However, after repeated injections of the dilute sample, the thiosulphate was found to gradually become symmetrical again and the peak eluting before chloride disappeared. It was strongly suspected that the tailing thiosulphate peak may in fact be due to the comigration of thiosulphate with an unidentified component in the sample. Initially it was not known which component or components in the sample could comigrate with thiosulphate. It was also puzzling why this behaviour had not been observed previously while analysing other samples. One difference between this and previous samples was that the white liquor which gave the problems had an orange-yellow colour, which is a good qualitative indicator of the presence of polysulphide in the sample. It was strongly suspected at this point that polysulphide anions may be comigrating with thiosulphate giving rise to the new peak before chloride. In addition, the disappearance of the peaks with time is consistent with the degradation of polysulphide, which is known to occur via a number of mechanisms, that will be discussed in detail in Chapter 4 of this thesis.

The nature of the problem encountered with white liquor samples is shown in Figure 3.11. As indicated, the upper electropherograms for a sample of white liquor known to contain polysulphide, while the lower electropherogram was obtained for a standard mixture of anions (without polysulphide present). As indicated, the thiosulphate peak in the liquor sample shows significant tailing and a new peak can be seen before chloride. In contrast, the thiosulphate peak in the standard mixture is very symmetrical and no peak is seen between thiosulphate and chloride. Analysis of several other samples known to contain polysulphide caused the same problems with the thiosulphate peak. The implication from these finding were that the presence of polysulphide in samples posed a serious interference in the analysis of thiosulphate and possibly in the analysis of chloride as well. The findings also indicated that it may be possible to determine polysulphide by CZE, provided a suitable electrolyte and analytical conditions could be found. Moreover, it was apparent that polysulphide anions possess a high mobility in the electrolyte being used.

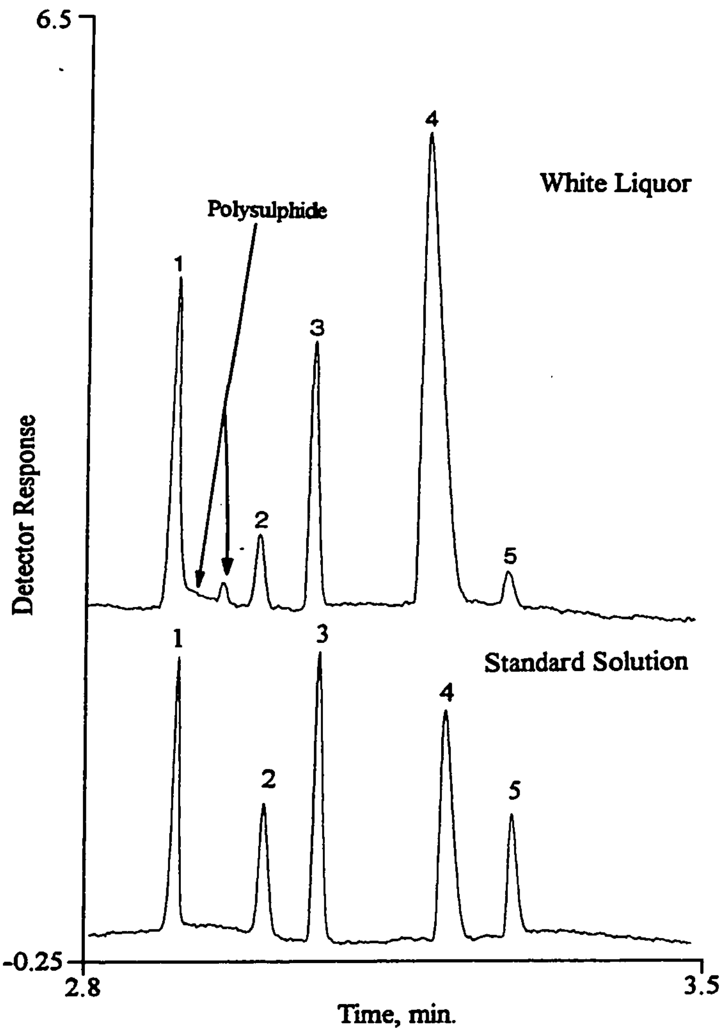


Figure 3.11. Separation of anions in a white liquor sample containing polysulphide (upper trace) and in a standard mixture (lower trace). The white liquor sample was diluted 1:1000 with He-sparged water and analysed immediately. Electrolyte: 4.5 mM chromate, 0.25 mM TTAOH, ambient pH 10.2. Separations performed using constant current (-16 µA). Detection at 275 nm. Peaks: Thiosulphate (1), chloride (2), sulphate (3), sulphide (4), sulphite (5). All solutes present at 10 mg/L in the standard mixture. See text and Experimental section for other conditions.

3.3.1.8.7 Development of an Electrolyte Suitable for Analysing Polysulphide-Containing Samples

The comigration of polysulphide with thiosulphate was a serious limitation in the utility and applicability of the existing method for determining sulphur species. One way to overcome this problem was to attempt to modify the existing electrolyte (in terms of chromate and/or TTAOH concentration) to obtain resolution of the anions of interest including polysulphide. The first step in this work was to prepare a series of electrolytes with varying concentrations of chromate (4-12 mM) and TTAOH (0.25-2 mM) and assess their ability to separate key anions of interest in a standard mixture. The results from these experiments are summarized in Table 3.6. As indicated in the table, chloride is well resolved from thiosulphate over a wide range of chromate and TTAOH concentrations. However, sulphate and sulphide, and in particular sulphide and oxalate, are much more sensitive to variations in electrolyte composition. Furthermore, it was discovered that the migration order of thiosulphate, oxalate

Table 3.6. Effect of chromate and TTAOH concentrations on the resolution of chloride, thiosulphate, sulphate, sulphide and oxalate. Separations were performed using the electrolyte compositions shown in the Table, with currents ranging between -16 to -20 μA. See text and Experimental for other conditions.

[Chromate] (mM)	[TTAOH] (mM)	pH	Resolution, Rs		
			chloride/thiosulphate	sulphate/sulphide	sulphide/oxalate
4	0.5	10.4	2.12	2.47	0.79
4.5	0.25	10.2	2.40	2.52	0.61
5	0.25	10.2	2.25	3.40	0.58
8	**2**	**11.3**	**2.16**	**1.39**	**1.52**
10	**2**	**11.4**	**2.31**	**1.56**	**1.57**
12	2	11.4	1.71	0.68	1.65

and carbonate were dramatically altered as the concentration of chromate and TTAOH increased. The best resolution of the three pairs of anions indicated in Table 3.6 was achieved using an electrolyte composed of 10 mM chromate and 2 mM TTAOH (ambient pH 11.4) with a separation current of -20 µA. A comparison of the separations achieved using the original and new electrolyte, and the effect of electrolyte composition on the order of migration of the anions is presented in Figure 3.12. As indicated in Figure 3.12 (A), the order of anion elution using the original electrolyte formulation was: **thiosulphate, chloride, sulphate, oxalate**, sulphide, sulphite, **formate and carbonate**. However, as shown in Figure 3.12 (B), the order of elution using the new electrolyte was: **chloride, thiosulphate, sulphate, sulphide**, oxalate, sulphite, **carbonate and formate.**

Using the optimized electrolyte system, the migration times of thiosulphate and oxalate increased and therefore their mobilities decreased relative to the other anions. The observed decrease in the migration time of thiosulphate and oxalate is likely due to non polar interactions rather than ionic interactions with TTAOH (a long chain alkyl quaternary amine). Thiosulphate and oxalate are relatively hydrophobic anions, and thus may associate more strongly with the non polar alkyl chain in the surfactant rather than with cationic (quaternary amine) group within the molecule. Non polar interactions between these anions and the surfactant would result in a net decrease in their mobilities relative to the other anions, which is what is observed in the current work. If thiosulphate and oxalate were interacting primarily with cationic sites in the surfactant, then the elution order of thiosulphate and oxalate with respect to the other anions would not change, since all anions are capable of interacting with the surfactant in this way.

Predictably, the migration time for carbonate (CO_3^{2-}) relative to formate decreased dramatically using the new electrolyte, for the reasons outlined below. As indicated in Table 3.6, the pH of the original electrolyte was about 10.2, which is close to the pK_a (10.3) of bicarbonate (HCO_3^-). Under these conditions, the observed carbonate peak is comprised of an approximately 1:1 mixture of HCO_3^- and CO_3^{2-}, resulting in a mixture having a net charge between -1 and -2. However, under the conditions that exist in the new electrolyte (ambient pH 11.4), the observed "carbonate" peak is primarily comprised of CO_3^{2-}, with a net charge of -2. Consequently, "carbonate" has a higher apparent charge-to-mass ratio in the new electrolyte and thus has a higher mobility, and therefore, a shorter migration time. It is worth noting that carbonate and formate are much better resolved using the new electrolyte, as indicated in Table 3.7. This is advantageous when analysing black liquor, since both ions are present at high levels in this type of sample.

Table 3.7. Separation of anions using optimized conditions. Electrolyte: 10 mM chromate, 2 mM TTAOH, separation current: -20 μA. See text and Experimental for other conditions.

Ion Pair	Resolution, Rs
chloride/thiosulphate	2.2
thiosulphate/sulphate	2.2
sulphate/sulphide	1.4
sulphide/oxalate	1.7
oxalate/sulphite	2.0
sulphite/carbonate	1.5
carbonate/formate	4.8

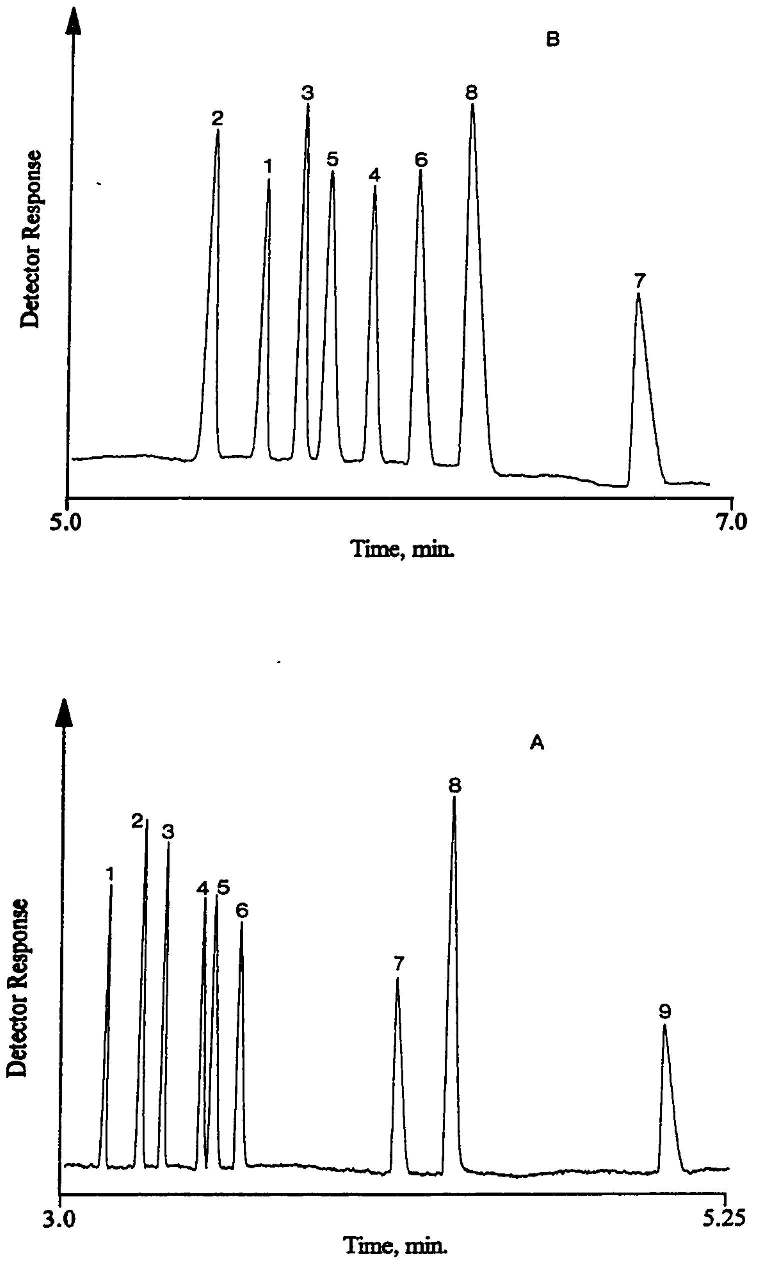


Figure 3.12. Separation of a standard mixture of anions using the original electrolyte formulation comprised of 4.5 mM chromate and 0.25 mM TTAOH (A) and the new electrolyte formulation comprised of 10 mM chromate and 2 mM TTAOH (B). Peaks: Thiosulphate (1), chloride (2), sulphate (3), oxalate (4), sulphide (5), sulphite (6), formate (7), carbonate (8) and acetate (9). See text and Experimental for other conditions.

In addition to the improved resolution, a further benefit of the new electrolyte is that it has a much higher ionic strength than the previous electrolyte, which provides enhanced analyte electrostacking. Electrostacking is the process by which anions move under the influence of the electric field from the sample zone within the capillary to the interface between the electrolyte and sample zones, forming a narrow band of analytes. The narrower the band of analytes is at the beginning of the analysis, the narrower the individual analyte bands will be as they separate during the run and thus the higher the efficiency of the separation. Electrostacking is enhanced when the conductivity of the sample plug is much lower than that of the electrolyte. This can be accomplished by using a high ionic strength electrolyte and by diluting the sample as much as possible prior to analysis. In the case of pulp and paper samples, analyte stability is generally enhanced by minimizing sample dilution, however in most cases, significant sample dilution is unavoidable.

3.3.1.8.8 **Analysis of Pulping Liquors Using the Optimized Electrolyte**

As demonstrated previously, the anions of interest were baseline resolved using the newly formulated electrolyte. However, it remained to be established whether polysulphide could be separated from the anions of interest in pulping liquors. To determine this, samples of black and white liquor, both of which had previously been found to contain polysulphide, were analysed using the optimized conditions.

As illustrated in Figure 3.13, all anions were well resolved in the pulping liquors and a peak between sulphide and oxalate, tentatively identified as polysulphide (P), was seen in the electropherograms of both samples. It is interesting to note that polysulphide behaves like thiosulphate and oxalate, in that its migration time increased significantly (or its effective

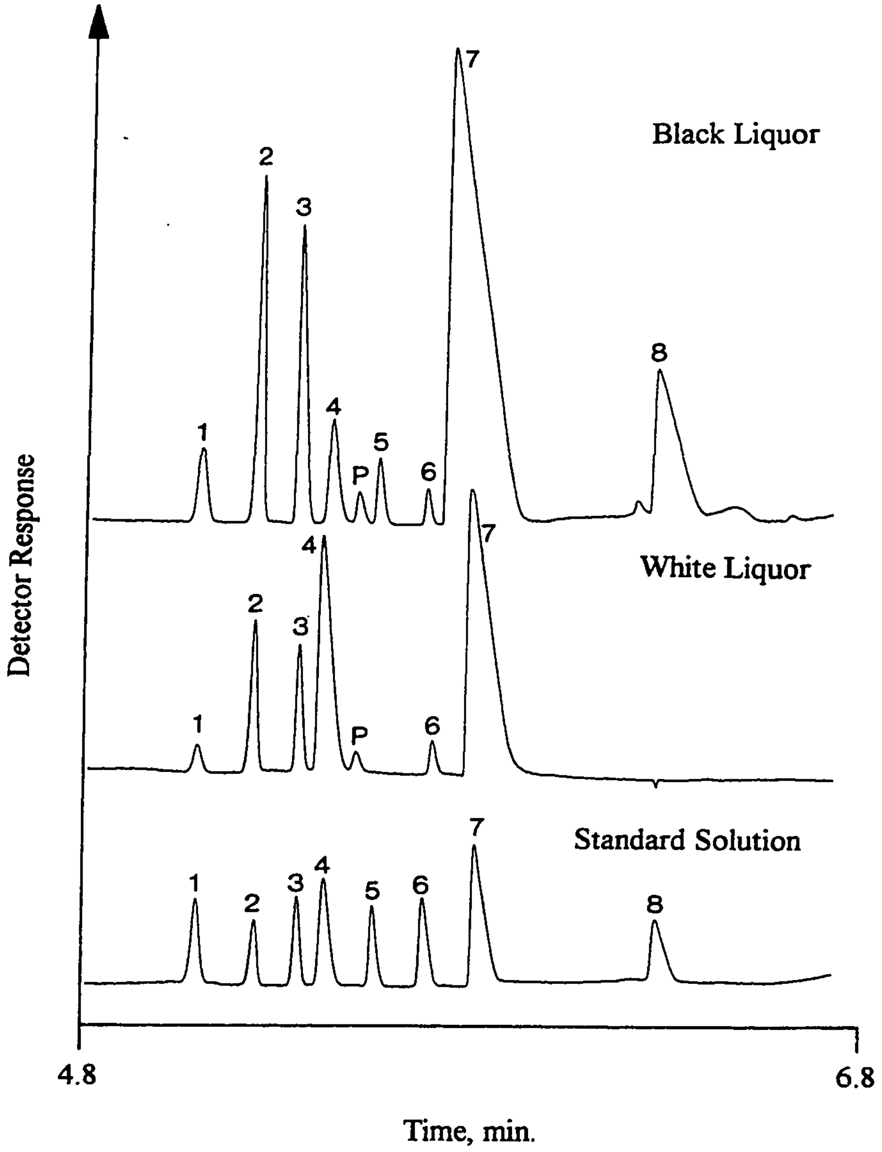


Figure 3.13. Separation of anions in a standard solution, white liquor and black liquor using optimized conditions. Electrolyte: 10 mM chromate, 2.0 mM TTAOH, ambient pH: 11.4, separation current: -22 μA. Peaks: Chloride (1), thiosulphate (2), sulphate (3), sulphide (4), polysulphide (P), oxalate (5), sulphite (6), carbonate (7), formate (8). The standard solution contained 5 mg/L of each anion. The white and black liquors were diluted 1:1000 and 1:250, respectively, in He-sparged water. See text and Experimental for other conditions.

mobility decreased) as the surfactant concentration was increased from 0.25 to 2 mM. This suggests that the surfactant is interacting strongly with polysulphide, probably in a manner similar to that described earlier for thiosulphate and oxalate. A possible mode of interaction between tetrasulphide (S_3S^{2-}), one of the major forms of polysulphide thought to exist in these solutions and the surfactant tetradecyltrimethylammonium cation is shown in Figure 3.14.

Figure 3.14. Illustration of a possible mode of interaction between tetrasulphide (S_3S^{2-}) and tetradecyltrimethylammonium cation in aqueous solution.

As indicated, it is believed that the charge on tetrasulphide is delocalized over the entire chain [48]. The polysulphide-surfactant complex depicted in Figure 3.14 would be expected to have a lower net negative charge and thus a lower effective mobility than free polysulphide. The expected result is a longer migration time for the complex compared to the free polysulphide, which is consistent with what was observed. Regardless of the exact mode in which the surfactant interacts with the various anions, the results illustrate how the selectivity of the separation of sulphide and polysulphide can be manipulated by simply varying the TTAOH concentration.

3.3.1.8.9 Repeatability of Migration Time, Peak Area and Linearity of Detector Response for Standard Mixtures of Anions

The repeatability of the migration time and peak area for the anions of interest was determined by performing six replicate injections of a mixed standard containing 5 mg/L of each ion. As shown in Table 3.8, excellent migration time repeatability was obtained for all anions with percent RSDs in the range 0.1 to 0.2 %. In addition, very good peak area repeatability was obtained for the various anions with percent RSDs in the range of 1-2 % range , with the exception of carbonate which had a percent RSD of 13 %. It was noticed that the peak area for carbonate gradually increased from run to run. This may be due to the build-up of carbonate in the sample over time by the reaction of atmospheric CO_2 with OH^- to form HCO_3^-. This reaction is unavoidable because of the relatively high alkalinity of the electrolyte (pH 11.4) and because of the fact that samples are introduced into the capillary (injected) by pressurizing the sample vial with room-air. The presence of carbonate in the electrolyte was found to affect the accuracy of the carbonate results. A detailed examination of the problem, along with a solution is presented later.

The linearity of the detector response was determined by performing duplicate injections of anion standards covering the concentration range of 1-50 mg/L. As indicated in Table 3.9, the response for each ion was linear over the specified concentration range, with correlation coefficients ≥ 0.9997 for each ion.

3.3.1.8.10 Repeatability of Migration Time and Peak Area for Anions in Liquor Samples

Replicate analyses of samples of white (WL), green (GL) and black liquor (BL) were performed to assess the repeatability of the migration times and peak areas for the various anions. White and green liquor samples were prepared in He-sparged water and repeatedly analysed over the course of an hour. The black liquor sample was diluted in He-sparged water containing 1 mg/mL of GSH and a low concentration of NaOH (ambient pH 11), and repeatedly analysed over the course of an hour.

Table 3.8. Repeatability of migration time and peak area for a standard mixture of anions using the optimized conditions. Each anion present at 5 mg/L. See text and Experimental for other conditions.

Anion	Migration Time (% RSD, n=5)	Peak Area (% RSD, n=5)
chloride	0.1	2.1
thiosulphate	0.1	1.0
sulphate	0.1	1.3
sulphide	0.1	1.0
oxalate	0.1	1.0
sulphite	0.1	0.9
carbonate	**0.2**	**12.5**
formate	0.1	1.9
hydroxide	0.2	1.2
acetate	0.2	1.3

As indicated in Table 3.10, excellent migration time repeatability (RSD≤0.3 %) was obtained for each ion in all samples examined. With the exception of sulphite, peak area repeatability was quite good (RSD 1-4%) for the remaining ions in each of the liquors studied. The peak area for sulphite was found to increase over time in each of the dilute liquor samples, which in turn explains the poor peak area repeatability (RSD, 10-30%).

Table 3.9. Linear regression results obtained from plots of peak area versus concentration for standard solutions of the various anions listed below, covering the concentration range 1-50 mg/L (1-50 mM for hydroxide). See text and Experimental for other conditions.

Anion	Slope	Intercept	Correlation Coefficient (R)
chloride	0.942	0.061	0.9999
thiosulphate	0.526	-0.053	0.9999
sulphate	0.770	0.047	0.9999
sulphide	1.106	-0.124	0.9999
oxalate	0.701	-0.039	0.9999
sulphite	0.995	-0.128	0.9998
carbonate	1.143	-0.211	0.9999
formate	0.958	-0.071	0.9999
hydroxide	10.213	-0.152	0.9997

What remains unclear however, is the exact cause of the increase in sulphite in dilute samples. One possible explanation is that polysulphide present in the original sample rearranges to elemental sulphur upon sample dilution. The sulphur then reacts with dissolved oxygen to form sulphite (cf. reaction 10). Another possible route to the formation of sulphite involves the reaction of sulphide with oxygen (cf. reaction 2). It should be remembered that sulphite is usually present at relatively low levels in the bulk (undiluted) liquor samples under consideration, and thus usually comprises a very small portion of the total sulphur present in the sample. Based on these findings, it is imperative that samples be analysed immediately after sample dilution in order to avoid large errors in the sulphite results.

Table 3.10. Migration time and peak area repeatability obtained from replicate analyses of samples of white, green and black liquor. See text and Experimental for other conditions.

Anion	Migration Time (% RSD, n=4)			Peak Area (% RSD, n=4)		
	WL	GL	BL	WL	GL	BL
chloride	0.1	0.1	0.1	2.1	3.2	1.1
thiosulphate	0.1	0.1	0.1	4.0	2.1	0.4
sulphate	0.1	0.1	0.1	2.5	2.1	0.3
sulphide	0.1	0.1	0.1	2.3	1.7	1.0
oxalate	-	-	0.2	-	-	2.3
sulphite	0.1	0.1	0.2	**26**	**10**	**21**
carbonate	0.3	0.4	0.1	1.7	1.4	1.6
formate	-	-	0.8	-	-	1.0
hydroxide	0.1	0.1	0.3	0.8	1.5	2.7

3.3.1.9 Quantitative Analysis of Anions in Kraft Pulping Liquors by CZE

The suitability of using the optimized CZE method for performing quantitative analysis was assessed by comparing the CZE results for hydroxide, chloride, thiosulphate, sulphate, sulphide, sulphite, oxalate, carbonate and formate in samples of green, white and black liquors, with those obtained by ion chromatography (IC) and by classical titrimetric methods. In addition, the accuracy of the CZE method was assessed by determining the recovery of the various anions from pulping liquors spiked with known concentrations of each analyte. The suitability of the CZE approach for determining carbonate is discussed first, followed by hydroxide and finally the remaining anions.

3.3.1.9.1 **Analysis of Carbonate**

During the course of the work it was discovered that the carbonate results obtained by the optimized CZE method were 5-25% lower than those obtained by well established and validated methods such as IC and coulometry. Since no reports on the use of CE for the quantitative analysis of carbonate have been published to date, there were few clues available to help explain why the results were low in the current work. After examining the literature further, it was hypothesized that a phenomenon known as "*reverse electrostacking*" [30] may be responsible for the low carbonate results. Reverse electrostacking, is as the name implies, the opposite of electrostacking. It 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 has been applied across the capillary. Since carbonate levels may vary considerably in the background electrolyte and because carbonate is an abundant analyte in the samples studied in this work, it was felt that reverse electrostacking of carbonate may be responsible for the low result obtained in this study. In indirect 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) will be smaller than expected, and thus a low carbonate result will be observed.

If reverse electrostacking were occurring, then much less or little reverse electrostacking should take place when the concentration of carbonate in the background was minimized. The majority of carbonate present in the electrolyte enters as a contaminant in the TTAOH, but additional carbonate is formed after each pressurization of the inlet side electrolyte vial, via the reaction of atmospheric carbon dioxide with hydroxide 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 should be significantly reduced, 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 contained 10 mM chromate but with different levels of TTAOH (2 and 0.2 mM). Plots of peak area versus carbonate concentration were linear over the range of 10-100 mg/L, with a correlation coefficient (R) of 0.9999 for both electrolytes. The relative standard deviation (RSD) of the migration time and peak area was 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 3.11, carbonate results obtained using the electrolyte with 0.2 mM TTAOH were in very good agreement with those obtained by IC and coulometry, while results obtained with 2 mM TTAOH were significantly lower. This indicates that reverse electrostacking is responsible for the low carbonate results found earlier. Unfortunately, the electrolyte optimized for the determination of carbonate is unsuitable for analysis of thiosulphate (due to comigration with polysulphide). Thus two electrolytes must be used to analyse all the anions of interest.. Interestingly, it was found that the carbonate peak was more symmetrical and migrated later when 0.2 mM instead of 2 mM

TTAOH was used, as illustrated in Figure 3.15. The reason for the improved symmetry is currently unknown. The longer migration time for carbonate is due to the lower pH of the electrolyte (the effect of electrolyte pH on the migration time of carbonate was discussed earlier).

Table 3.11. Comparison of carbonate results obtained for kraft white (WL), green (GL) and black (BL) liquors by IC, coulometry and CZE. Two electrolytes containing 10 mM chromate and the concentrations of TTAOH specified in the Table were used in the CZE work. See text and Experimental for other conditions.

Sample	[Carbonate], mg/L			
	IC	Coulometry	CZE1) (2 mM TTAOH)	CZE2) (0.2 mM TTAOH)
WL-A	14426	14000	10741	14050
WL-B	19414	19440	14584	19250
GL-A	70447	71900	58074	71053
GL-B	79308	81830	62534	82127
BL-A	14900	15100	13640	14815
BL-B	10200	10400	8990	9983

1) Capillary inlet electrolyte replaced after 5-7 runs; separation current: -20 μA.
2) Capillary inlet electrolyte replaced after each run; separation current: -25 μA.

3.3.1.9.2 Analysis of Hydroxide

The hydroxide result obtained by CZE and titrimetry is comprised of the hydroxide originating from the NaOH and from half the Na_2S present in the sample, as illustrated by reactions 11 and 12. In the pulp and paper industry, this is commonly referred to as the effective alkalinity (EA) of the liquor, and is usually expressed in g Na_2O/L basis rather than on an NaOH basis.

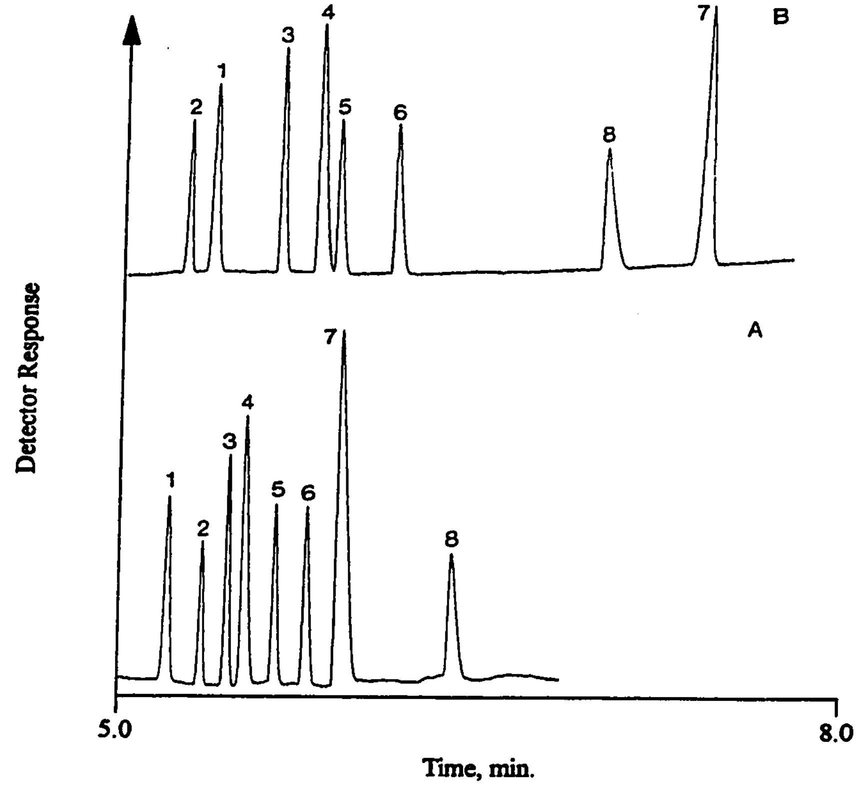


Figure 3.15. Effect of TTAOH concentration on the separation of anions in a standard mixture. Electrolyte compositions: 10 mM chromate, 2 mM TTAOH (A); 10 mM chromate, 0.2 mM TTAOH (B). Peaks: Chloride (1), thiosulphate (2), sulphate (3), sulphide (4), oxalate (5), sulphite (6), carbonate (7), formate (8). Each anion present at 5 mg/L. See text and Experimental for other conditions.

$$NaOH + H_2O \rightleftharpoons Na^+ + OH^- + H_2O \qquad (11)$$

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH \qquad (12)$$

The hydroxide, sulphide and carbonate concentrations of white and green liquors are commonly determined by a potentiometric titration method referred to as the ABC titration [11]. In this titration, an aliquot of sample is diluted in water and an excess of $BaCl_2$ is added to precipitate carbonate as $BaCO_3$. The sample at this point contains hydroxide and sulphide in solution, with barium carbonate present as a suspended precipitate. The sample is then titrated with a strong acid such as HCl to the first equivalence point (A), which yields the EA result. Next, excess formaldehyde (CH_2O) is added to the sample to form an adduct with hydrosulphide, with a release of hydroxide ($CH_2O + HS^- + H_2O \rightleftharpoons HO\text{-}CH_2\text{-}SH + OH^-$). The released hydroxide is equivalent to the HS^- originally present in the sample. The released hydroxide is then titrated to the second equivalence point (B), which represents the sulphide content of the sample. The titration is continued until the third endpoint (C) yielding the carbonate concentration of the sample ($BaCO_3$ (s) + 2 HCl $\rightleftharpoons$ $BaCl_2$ + H_2CO_3). With certain precautions and great care, this titration method can also be applied to black liquors, but only for determination of EA [15].

In the current work, the concentration of hydroxide in white, green and black liquors was determined by CZE using the optimized electrolyte system consisting of 10 mM chromate and 2 mM TTAOH. For CZE analyses, aliquots of white, green and black liquors were diluted

1:1000 (1:500 for black liquors) in He-sparged water, filtered through a 5 μm filter and analysed immediately. The hydroxide, sulphide and carbonate contents of white and green liquors, and the hydroxide content of the black liquors were determined by the ABC titration method [11]. In the case of the black liquor sample, barium chloride was added to the sample to precipitate barium carbonate. A portion of the sample was then passed through a 5 μm filter and titrated to pH 10.5 to obtain the EA result.

As indicated in Table 3.12, the NaOH (EA) results obtained by CZE and titrimetry differ by only about 5% for most of the samples studied. These results indicate that CZE can be used to accurately determine the EA content of kraft liquors in a much more convenient manner than is possible by conventional methods.

Table 3.12. Comparison of CZE and titrimetry results for sodium hydroxide (EA) for kraft liquors. The electrolyte used for CZE analyses was comprised of 10 mM chromate and 2 mM TTAOH. Titrations were done according procedures described in references 11 and 48. See text and Experimental for other conditions.

Sample	[NaOH], mM	
	CZE	ABC Titration
WL-A	2650	2702
WL-B	2239	2340
GL-A	850	880
GL-B	973	972
BL-A	280	300
BL-B	257	275

The major advantage of the CZE method is that very little sample preparation is required and a direct measurement of the EA is possible from the analysis. In the case of white and green liquors, the other anions of interest (with the exception of carbonate) can be determined in the same run. In the case of black liquors, chloride, oxalate and formate can be analysed in the same run. The analysis of sulphur species in black liquor must be done with GSH added to the sample to stabilize sulphide, as described earlier.

The concentration of TTAOH (and thus the hydroxide concentration) in the electrolyte was found to have a significant effect on the shape of the hydroxide peak for all types of kraft liquors examined. To illustrate this, a sample of white liquor was analysed by CZE using two electrolytes with the same chromate concentration (10 mM), but with different TTAOH concentrations (2 mM and 0.25 mM). Both separations were carried out with at current of -20 μA. As indicated in Figure 3.16, the hydroxide peak obtained with the electrolyte containing 2 mM TTAOH exhibits some fronting, but is much more symmetrical than the hydroxide peak obtained with the electrolyte containing 0.25 mM TTAOH. Since the main difference in the two electrolytes is the pH, it appears that this parameter has 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. At this time, the observed changes in the hydroxide peak cannot be explained. As mentioned earlier, the same variations in hydroxide peak shape were observed with green and black liquors and therefore, sample type does not appear to affect hydroxide peak shape.

3.3.1.9.3 Determination of Sulphur Species, Chloride, Oxalate and Formate

3.3.1.9.3.1 Analysis of Black Liquor Samples

Black liquor is a complex sample containing hundreds of organic and several inorganic compounds. In addition, quantitative analysis of oxysulphur anions in black liquor is complicated by the oxidation of sulphide (and polysulphide) in the presence of oxygen and

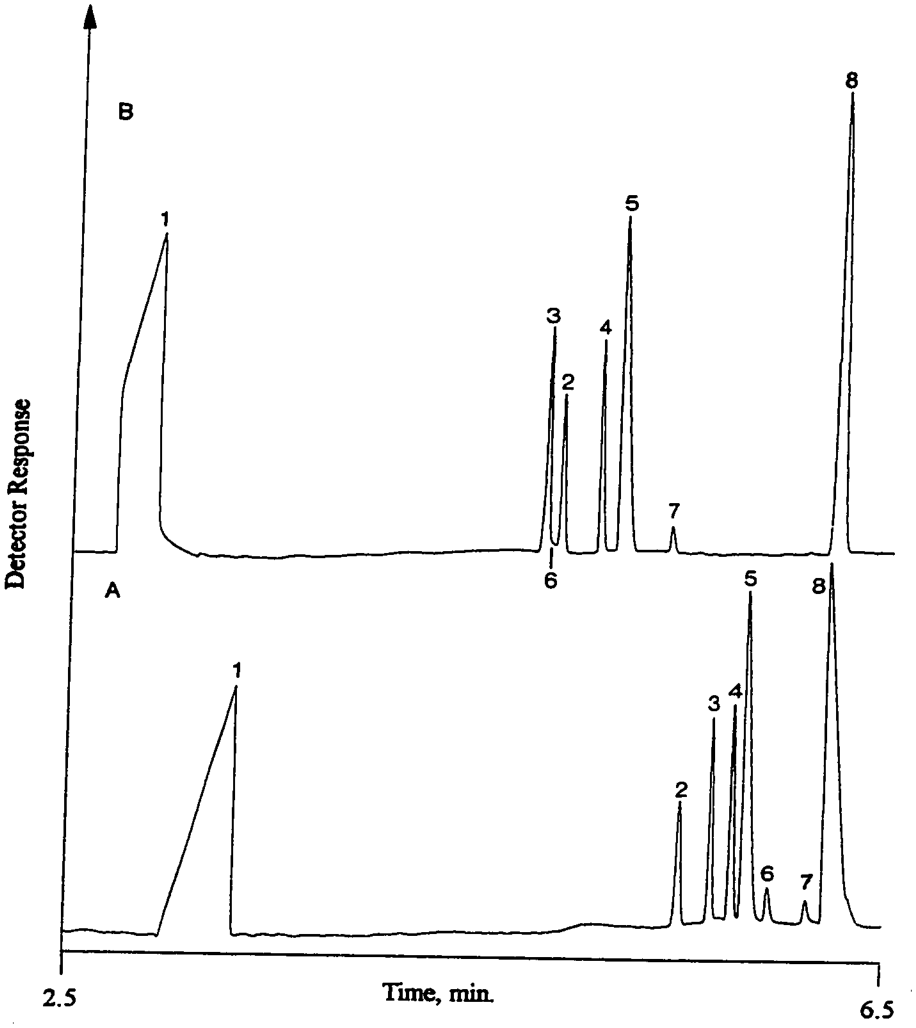


Figure 3.16. Effect of electrolyte composition on the shape of the hydroxide peak, as illustrated with a white liquor sample. Separations were done with two electrolyte containing the same chromate concentration (10 mM) but with different TTAOH concentrations (2 mM (A) and 0.25 mM (B)). The separation current was -20 µA in each case. Peaks: Hydroxide (1), chloride (2), thiosulphate (3), sulphate (4), sulphide (5), polysulphide (6), sulphite (7) and carbonate (8). See text and Experimental for other conditions.

quinones which lead to the formation of a number of oxysulphur species, as described earlier. Moreover, the classical titrimetric and ion chromatography methods developed to date are tedious and time consuming or are unsuitable for determining the various anions using a single set of conditions. Consequently, the quantitative analysis of the key anions in this type of sample can only be done by employing several methods.

Using the optimized CZE conditions and GSH to stabilize sulphide, the analysis of the sulphur anions in black liquor becomes much simpler and faster than conventional methods. In addition, sulphide and the major oxysulphur species can now be monitored simultaneously by CZE with little sample preparation. The quantitative nature of the CZE method was assessed by comparing the results obtained by CZE for the various oxysulphur species and other anions such as chloride, oxalate and formate with those obtained by ion chromatography [17]. The sulphide result obtained by CZE was compared to that obtained by potentiometry, which utilizes a Ag/AgS ion-specific electrode (ISE) and a mercuric chloride titrant [13]. As indicated in Table 3.13, the CZE results obtained for the various anions were in good agreement with those obtained by IC and potentiometry. These results indicate that CZE may be used to rapidly quantify the major anions. To my knowledge, this is the first work to demonstrate that CZE is suitable for the quantitative analysis of inorganic anions in kraft liquors. It should be remembered that it is imperative that black liquor be prepared in the presence of sufficient GSH to stabilize sulphide, and that the protocol developed for sample preparation outlined in this work be followed rigorously.

Table 3.13. Analysis of sulphur species, chloride and organic anions in black liquor by CZE, IC and titrimetry. CZE separations were performed using an electrolyte comprised of 10 mM chromate, 2 mM TTAOH and a current of -20 μA. See text and Experimental for other conditions.

Anion	[Anion], mg/L		
	CZE	IC	Titrimetry (ISE)
thiosulphate	5727	5854	-
sulphate	1508	1525	-
sulphide	3250	-	3387
sulphite	421	398	-
chloride	126	139	-
oxalate	455	455	-
formate	5968	5712	-

3.3.1.9.3.2 Analysis of White and Green Liquor Samples

The determination of anions in white and green liquors is somewhat less complicated than it is for black liquors because the former samples are free from organic compounds such as quinones, which can oxidize sulphide to oxysulphur species. However, white and green liquors may contain significant concentrations of polysulphides, which are inherently unstable in dilute samples (or under conditions of low ionic strength and low pH) and are readily oxidized to several oxysulphur species, as described earlier. Furthermore, polysulphide has been found to comigrate with thiosulphate, using the original electrolyte formulation. The suitability of the optimized CZE method for determining sulphide, oxysulphur species, and chloride was assessed by comparing the CZE results obtained from the analysis of several white and green liquors with those obtained by titrimetry and IC. For CZE analysis, samples were diluted in He-sparged water (1:1000) and analysed immediately. The white liquors had a faint orange colour, indicating the presence of low levels of polysulphide.

As indicated in Table 3.14, sulphide results obtained by CZE were within 1-2% of those obtained by the titrimetric methods. These result indicate that the CZE method is suitable for determining sulphide in white and green liquors. The concentration of oxysulphur species and chloride were also determined in the same samples by CZE and IC.

Table 3.14. Analysis of sulphide in white (WL) and green (GL) liquors by CZE and titrimetry. CZE separations were performed using an electrolyte composed of 10 mM chromate and 2 mM TTAOH, with a current of -20 μA. See text and Experimental for other conditions.

Liquor Sample	[Sulphide], mg/L			Ratio of CZE to Titrimetry	
	CZE	Titrimery (ABC)	Titrimetry (ISE)	CZE/ABC	CZE/ISE
WL-D	9631	9800	9750	0.98	0.99
WL-E	11021	11159	11287	0.99	0.98
GL-E	11877	11718	11435	1.01	1.04
GL-F	15733	15820	15752	0.99	1.00
GL-G	17411	17569	17721	0.99	0.98

As indicated in Table 3.15, the CZE and IC results for the oxysulphur species and for chloride are generally in good agreement. The largest discrepancies between the two 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 polysulphide during sample dilution to form sulphite, by the mechanism described earlier. One other problem with the sulphite analysis is the low level of sulphite present in the sample. After the sample has been diluted 1:1000, the concentration of sulphite is about 0.25-0.3 mg/L. At this concentration, sulphite is near the detection limit of the CZE method. It probably would have been more appropriate to reanalyse for sulphite using a dilution factor of 1:500.

Table 3.15. Analysis of oxysulphur species and chloride in white and green liquor by CZE and IC. CZE separations were performed using an electrolyte composed of 10 mM chromate, 2 mM TTAOH, with a current of -20 μA. See text and Experimental for other conditions.

Anion	[Anion], mg/L					
	WL-D		**WL-E**		**GL-E**	
	CZE	IC	CZE	IC	CZE	IC
thiosulphate	3195 ± 45	3140 ± 62	4050 ± 75	4113 ± 36	3772 ± 52	3586 ± 31
sulphate	5572	5745	4150	4287	3257	3260
sulphite	660	598	449	480	259	305
chloride	1021	1098	722	780	823	792

To determine the accuracy of the CZE method, samples of green and white liquor were analysed before and after the addition of known amounts of sulphide, oxysulphur anions and chloride. As indicated in Table 3.16, the recoveries ranged between 95 and 115% for all anions studied. The anion results obtained by CZE thus far are in good agreement with those obtained by classical methods such as titrimetry and IC. These findings show that the CZE method developed in this work provides quantitative results for carbonate, hydroxide, sulphur species, chloride, oxalate and formate in kraft process liquors.

Table 3.16. Recovery of chloride and oxysulphur anions from green and white liquors. Each sample was diluted and spiked with the concentration indicated below. Three replicate analyses were performed on the original samples and spikes were performed in duplicate at each level indicated. Separations were performed using an electrolyte comprised of 10 mM chromate, 2 mM TTAOH and with a current of -20 μA. See text and Experimental for other conditions.

Anion	Anion Concentration (mg/L)			Recovery (%)
	Original (mean ± SD) n = 3	Added	Found (mean ± AD) n = 2	
GL-E				
chloride	823 ± 39	200 400	203 ± 7 416 ± 12	103 ± 2 104 ± 3
thiosulphate	3772 ± 52	2000 4000	2120 ± 60 4320 ± 120	106 ± 3 108 ± 3
sulphide	11541 ± 248	2000 4000	1980 ± 40 3800 ± 80	99 ± 2 95 ± 2
sulphate	3257 ± 124	2000 4000	2120 ± 80 4160 ± 120	106 ± 4 104 ± 3
sulphite	259 ± 21	200 400	214 ± 8 448 ± 32	110 ± 11 112 ± 12
WL-D				
chloride	960 ± 45	200	200 ± 2	100 ± 1
thiosulphate	3428 ± 45	2000	2127 ± 32	106 ± 2
sulphide	9307 ±113	3000	3000 ± 91	101 ± 2
sulphate	5827 ± 32	2000	2060 ± 40	103 ± 2
sulphite	750 ± 70	200	230 ± 29	115 ± 15

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CHAPTER 4

ANALYSIS OF SULPHUR SPECIES AND SPECIATION OF POLYSULPHIDE IN KRAFT MILL PULPING LIQUORS BY CAPILLARY ELECTROPHORESIS USING DIRECT UV-DETECTION

4.1 Introduction

The goal of kraft and other chemical pulping processes is to degrade and dissolve away the lignin present in the wood, and to leave behind most of the cellulose and hemicellulose in the form of intact fibres. In the kraft process, delignification has traditionally been accomplished by heating (cooking) wood chips in a solution containing primarily NaOH and Na_2S (known as white liquor), at temperatures of 170-180°C for 2-3 hours [1,2]. Under these conditions, a significant proportion of the lignin and unfortunately, a significant portion of the hemicellulose, as well as a small percentage of the cellulose, is extracted and/or degraded, and removed in the black liquor. Consequently, the yield of pulp from the process is reduced as a result of the carbohydrate loss.

In an effort to improve the efficiency of the process, white liquor containing Na_2SS_n ($4 \geq n \geq 1$) and/or anthraquinone is increasingly being used [3-8]. The replacement of some of the sulphide with polysulphide results in improved retention of holocellulose (cellulose and hemicellulose) within the fibres and thereby an increase in the yield of pulp from the pulping process. The increase in holocellulose or pulp yield is due to the ability of polysulphide to oxidize the aldehyde functions (present as end-groups) in carbohydrate chains to carboxyl groups, rendering them stable against endwise "peeling" reactions, which occur under the highly alkaline conditions that exist during pulping.

Polysulphide is generally produced on-site at the paper mill by a controlled, catalysed air oxidation of sulphide present in the white liquor, as illustrated in reaction 1 [4].

$$(2n+2)HS^{-}+nO_2 \rightleftharpoons 2S_nS^{2-}+2(n-1)OH^{-}+2H_2O \tag{1}$$

Although not done commercially, polysulphide can also be produced by reacting sulphur with alkaline sulphide solution as indicated in reaction 2.

$$nS^{o}(s) + HS^{-} + OH^{-} \rightleftharpoons S_{\bar{n}}S^{2-} + H_2O \tag{2}$$

Where $\bar{n}$ is the average number of sulphur atoms in the chain. The average chain length is thought to be controlled by the variable B, as shown below [8].

$$B = \frac{[HS^{-}][OH^{-}]}{[S^{o}]} \tag{3}$$

The average $\bar{n}$ value tends to decrease with increasing B value [8] and is thought to vary between 1 to 4 [8]. Therefore, varying proportions of polysulphide species such as SS^{2-}, S_2S^{2-}, S_3S^{2-}, and S_4S^{2-} may be present in solution simultaneously [9]. Based on the relationship above, it is believed that short chain polysulphide forms are favoured in highly alkaline solutions containing low levels of sulphur, and long chain forms would be more abundant in solutions with low alkalinity and/or high levels of sulphur. Teder has postulated that an equilibrium exists between aqueous polysulphide ions of various chain lengths as indicated in reaction 4 [10].

$$S_iS^{2-} + S_jS^{2-} + H_2O \rightleftharpoons S_{i+j}S^{2-} + HS^- + OH^- \qquad (4)$$

As indicated in reaction 4, it is thought that high alkalinity and sulphidity favour the formation of polysulphide with shorter average chain lengths. This reaction also indicates that dilution of samples containing polysulphide leads to a decrease in pH and thus an alteration of the original distribution of the species present in the sample. The chemistry of polysulphide is complicated further by the autoxidation of polysulphide to thiosulphate, as indicated in reaction 5 [4].

$$2S_nS^{2-} + (n+2)O_2 + 2(n-1)OH^- \rightleftharpoons (n+1)S_2O_3^{2-} + (n-1)H_2O \qquad (5)$$

Moreover, during the production of polysulphide via the air oxidation of sulphide, a number of unwanted oxysulphur species, such as thiosulphate, sulphite and sulphate are produced, as shown in reactions 6-8.

$$2HS^- + 2O_2 \rightleftharpoons S_2O_3^{2-} + H_2O \qquad (6)$$

$$2HS^- + 3O_2 \rightleftharpoons 2SO_3^{2-} + 2H^+ \qquad (7)$$

$$2SO_3^{2-} + O_2 \rightleftharpoons 2SO_4^{2-} \qquad (8)$$

Comprehensive reports on sulphide/polysulphide chemistry and on the analytical methodology developed for determining sulphide and polysulphide in kraft mill liquors have appeared [11-13]. While a number of reliable methods have been developed for determining sulphide in kraft mill liquors, far fewer and less direct methods have been developed for quantifying polysulphide. One of the major indirect methods for determining polysulphide (P) involves the reaction of SO_3^{2-} with polysulphide to form $S_2O_3^{2-}$, HS^- and OH^-, as shown below.

$$S_nS^{2-} + nSO_3 + H_2O \rightleftharpoons nS_2O_3^{2-} + HS^- + OH^- \qquad (9)$$

Measurement of the thiosulphate produced can be done by potentiometric titration [14] or by IC [15] before and after the reaction to obtain the concentration of thiosulphate formed from the polysulphide. This then allows for the calculation of the polysulphide concentration in the original sample. More direct methods for determining polysulphide include UV spectroscopy [16] and gas chromatography [11]. The UV-based method is only suitable for obtaining the total polysulphide concentration and provides no information on the forms of polysulphide present in solution. The GC method is based on the decomposition of polysulphide to elemental sulphur (S^0) in a buffered aqueous solution followed by derivatization with triphenylphosphine (TPP) to form the triphenylphosphine sulphide (TPPS). TPPS is isolated by extraction into toluene followed by GC analysis. This approach obviously only gives the total zero valent sulphur present in the polysulphide, but provides no information on the forms of polysulphide originally present.

Recently, CZE with direct UV-detection has been applied to the separation of sulphide and selected oxysulphur (sulphite and thiosulphate) anions in leather industry effluents [17] and in corrosion studies of steel [18]. The former paper describes the use of an electrolyte composed of 10 mM sodium sulphate and an electroosmotic flow modifier known as OFM anion-OH, while in the latter paper, an electrolyte comprised of 25 mM sodium chloride and OFM anion-OH was used. However, only the former authors have demonstrated that their method is suitable for quantitative analysis (sulphide only). Neither groups has demonstrated that their method is suitable for determining thiosulphate or sulphite nor is it clear that their methods are suitable for analysing complex samples such as those found in the pulp and paper industry.

One of the potential advantages of using CZE with direct UV detection for the analysis of anions is that very simple electropherograms should be obtained. This is expected since very few anions possess a significant absorbance in the UV. Unlike indirect detection, direct UV allows for the use of high ionic strength electrolytes (either buffered or unbuffered), without sacrificing the quality of the separation. Because high ionic strength electrolytes help enhance electrostacking, it should be possible to analyse high ionic strength (and high pH) samples such as kraft liquors with little or less sample dilution. The ability to analyse relatively concentrated liquors is extremely important if polysulphide-containing samples are to be examined since polysulphide is more stable under high ionic strength/pH conditions.

The objectives of the current work were to attempt to develop a CZE method with direct UV-detection suitable for determining sulphide, sulphite, thiosulphate and hydroxide, and to assess the suitability of the method for speciating polysulphide in kraft white liquors.

4.2 Experimental

4.2.1 Materials

4.2.1.1 Chemicals

Analytical grade anhydrous sodium sulphate and sodium sulfide nonahydrate were obtained from Mallinckrodt (St. Louis, MO, USA). Tetradecyltrimethylammonium bromide (TTAB), sodium hydroxide, sodium sulphite, sodium thiosulphate and sodium carbonate were analytical or ACS grade reagents from Aldrich (Milwaukee, WI, USA). Sodium tetrasulphide (Na_2S_4, 90-95% purity) was obtained from Alfa Aesar (Ward Hill, MA, USA). Standard 1 M NaOH was obtained from Fisher Scientific (Montreal, Quebec, Canada). Water used throughout this work was from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

4.2.1.2 Apparatus

Capillary electrophoresis experiments were performed with two instruments. Initially, studies were conducted with a Crystal 310 CE instrument equipped with a model 4225 UV/Vis detector from Thermo Bioanalysis (Franklin, MA, USA). The Instrument control and data acquisition were conducted using Thermo Bioanalysis software (version 1.3 beta) and the 4880 data acquisition package (version 3.0). The data acquisition rate was set to 20 Hz. For studies conducted with the Crystal CE, fused-silica capillary tubing of 75 μm i.d x 363 μm o.d was purchased from Polymicro Technologies (Phoenix, AZ, USA). Individual capillaries with a total length of 80 cm (Lt) and effective length to detector of 65 cm (Ld) were cut from the bulk tubing with the aid of a ceramic knife. A 5 mm wide detection window was created by burning off the polyimide coating with a butane lighter. The window was cleaned with a lens tissue wetted with acetone prior to use.

In later studies, work was performed with a model G1600A HP^{3D} capillary electrophoresis instrument equipped with diode-array detection from Hewlett-Packard (Montreal, Quebec, Canada). The HP 1601A CE chemstation was used for instrument control, data acquisition and data analysis. The data acquisition rate was set at 20 Hz. A HP extended light path ("bubble" cell) capillary with an optical pathlength of 150 μm was used in work involving the HP instrument [19]. The capillary dimensions were: 50 μm i.d. x 375 μm o.d. x 65 cm (Ld =56 cm). An alignment interface containing an optical slit matched to the capillary was also obtained from Hewlett-Packard.

All separations were performed using the constant current mode, at ambient room temperature, with a negative polarity applied to the inlet end of the capillary. For studies utilizing the 75 μm i.d. capillary, samples were injected using pressures of 10-25 mBar for 10-15 seconds. For studies utilizing the 50 μm i.d. capillary, samples were injected using pressures of 10 mBar for 20-30 seconds.

4.2.2 **Methods**

4.2.2.1 **Electrolyte Preparation**

The background electrolyte used for direct UV detection was comprised of analytical grade sodium sulphate and teradecyltrimethylammonium hydroxide (TTAOH). Running electrolyte solution was prepared daily by diluting stock 100 mM Na_2SO_4 and 20 mM TTAOH solutions with Milli-Q water. Stock TTAOH solution was prepared as described in Chapter 3. Prior to use, the electrolyte was degassed by sonication for 5 minutes and then filtered through a 0.5 μm syringe filter (Millex-LCR, Millipore) into a polypropylene bottle

(Nalgene).

For work done with the Thermo instrument, ca. 3.75 mL of filtered electrolyte was delivered to several 4 mL glass autosampler (capillary inlet) vials with the aid of a pipette. The capillary outlet vial in the Thermo instrument was filled with ca. 35 mL of electrolyte and used without replenishment throughout the day. For work done with the HP instrument, ca. 0.65 mL of filtered electrolyte was delivered to several 1 mL polypropylene vials with the aid of a pipette. Separate capillary inlet and outlet vials were used for each analysis.

4.2.2.2 **Capillary Cleaning Protocol**

Capillary cleaning was done according to the protocol described in Chapter 2.

4.2.2.3 **Standards and Solutions**

Standard stock solutions of the various anions and mixed standards were prepared as described in Chapter 2.

Stock sodium tetrasulphide solution (ca. 1000 mg/L S_4^{2-}) was prepared daily by diluting technical grade sodium tetrasulphide in He-sparged 1 M NaOH. Dilute standards were prepared by dilution of stock with He-sparged 0.25 M NaOH and analysed without delay.

All solutions and samples were prepared and stored in polmethylpentene (PMP) flasks (Fisher Scientific).

4.2.2.4 **Preparation of Samples**

Samples of green liquor as well as oxidized and unoxidized white liquor were obtained from Canadian kraft mills and stored at 25 °C in the dark. Samples were diluted in He-sparged water, filtered through a 25 mm x 5 μm PTFE membrane syringe filter (Chromatography

Sciences Company (CSC), St. Laurent, Quebec, Canada) and analysed immediately.

4.3 Results and Discussion

4.3.1 Electrolyte Development and Selection of Detection Wavelength

Previous work by Font et al. has shown that sulphide, thiosulphate and sulphite can be separated using an electrolyte composed of 10 mM sodium sulphate with 0.5 mM TTAOH [17]. Because of the high concentration of sulphate present in kraft white liquor (3-5 g/L) and because of the low absorptivity of sulphate in the UV, it was decided that a sodium sulphate-based electrolyte might be best suited for our application. In the current work, it was felt that the ionic strength of the electrolyte (sulphate concentration) should be kept as high as possible to allow the analysis of relatively concentrated samples of white liquor.

Initially, the suitability of using an electrolyte containing 20 mM sodium sulphate and 1.25 mM TTAOH for the separation of sulphide, thiosulphate and sulphite was assessed. The choice of detection wavelength was less straightforward however, because of the varied spectroscopic characteristics of the analytes of interest. For example, it is known that sulphide possesses a strong absorption maxima centered near 230 nm (cf. Figure 3.1 in this work), but both sulphite and thiosulphate absorb only moderately between 185 and 230 nm [18]. To allow for the simultaneous detection of all analytes, a compromise between sensitivity, signal-to-noise and detectability was made. Consequently, a wavelength of 205 nm was chosen for the initial evaluation. It should be noted that the capillary cleaning protocol developed for indirect detection was also employed in this work.

As indicated in Figure 4.1, very good resolution of the sulphur species was obtained using an electrolyte composed of 20 mM sodium sulphate and 1.25 mM TTAOH. In addition, the choice of detection wavelength (205 nm) proved to be well suited to the detection of all species.

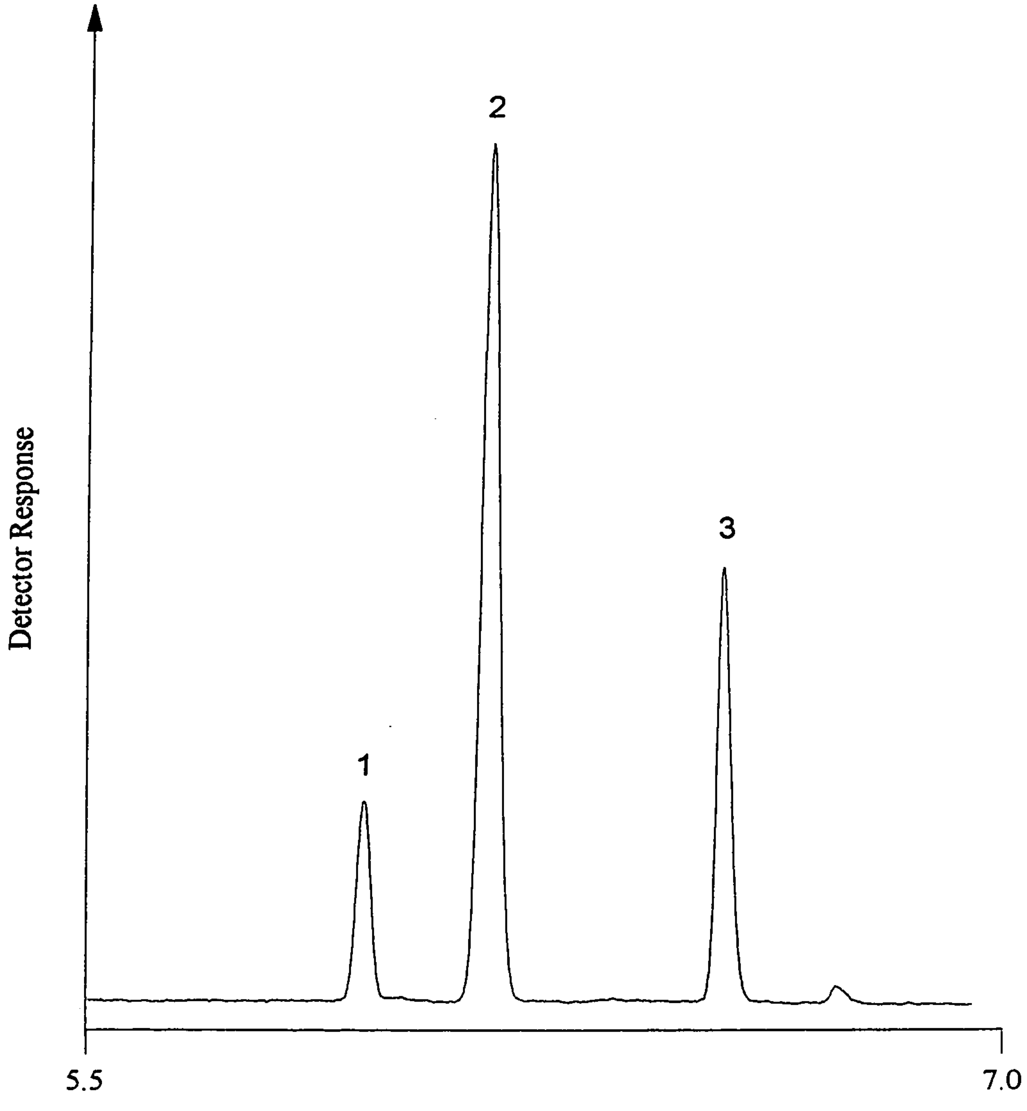

Figure 4.1. Separation of a standard mixture containing 10 mg/L each of thiosulphate (1), sulphide (2) and sulphite (3). Electrolyte consisted of 20 mM sodium sulphate and 1.25 mM TTAOH. Separation was done using constant current (-28 μA). See text and Experimental for other conditions.

4.3.2 Analysis of Sulphur Anions and Polysulphide in White Liquor and Sodium Tetrasulphide

The next step in our work was to determine if the optimized electrolyte system was suitable for separating the three sulphur anions and polysulphide. This was done by analysing a standard solution of the three sulphur anions (as described above), along with a solution of commercially available sodium tetrasulphide and a sample of oxidized white liquor (known to contain polysulphide, PS). All solutions were prepared in He-sparged water and analysed immediately.

As shown in Figure 4.2, thiosulphate, sulphide and sulphite were well resolved in the standard mixture, as expected. However, the tetrasulphide and oxidized white liquor samples were found to contain two additional peaks (labelled PS-1 and PS-2),both of which are polysulphide anions. As indicated, the PS ions eluted between thiosulphate and sulphide and the PS-2 ion was poorly separated from sulphide. In addition, the ratio of PS-1 to PS-2 was much higher in the oxidized white liquor sample than in the tetrasulphide sample. The results of this work showed several things: 1) at least two forms of polysulphide could be detected using the existing CZE method, 2) the electrolyte formulation was not optimized for the simultaneous analysis of sulphur anions and polysulphide and 3) perhaps the selectivity of the separation could be enhanced by increasing the surfactant concentration, as was done in the indirect detection scheme described in Chapter 3.

4.3.3 Optimization of Electrolyte for the Separation of Thiosulphate, Sulphide and Sulphite

The effect of TTAOH on the separation of sulphur species was assessed by preparing a series of electrolytes containing 20 mM Na_2SO_4 with concentrations of TTAOH ranging

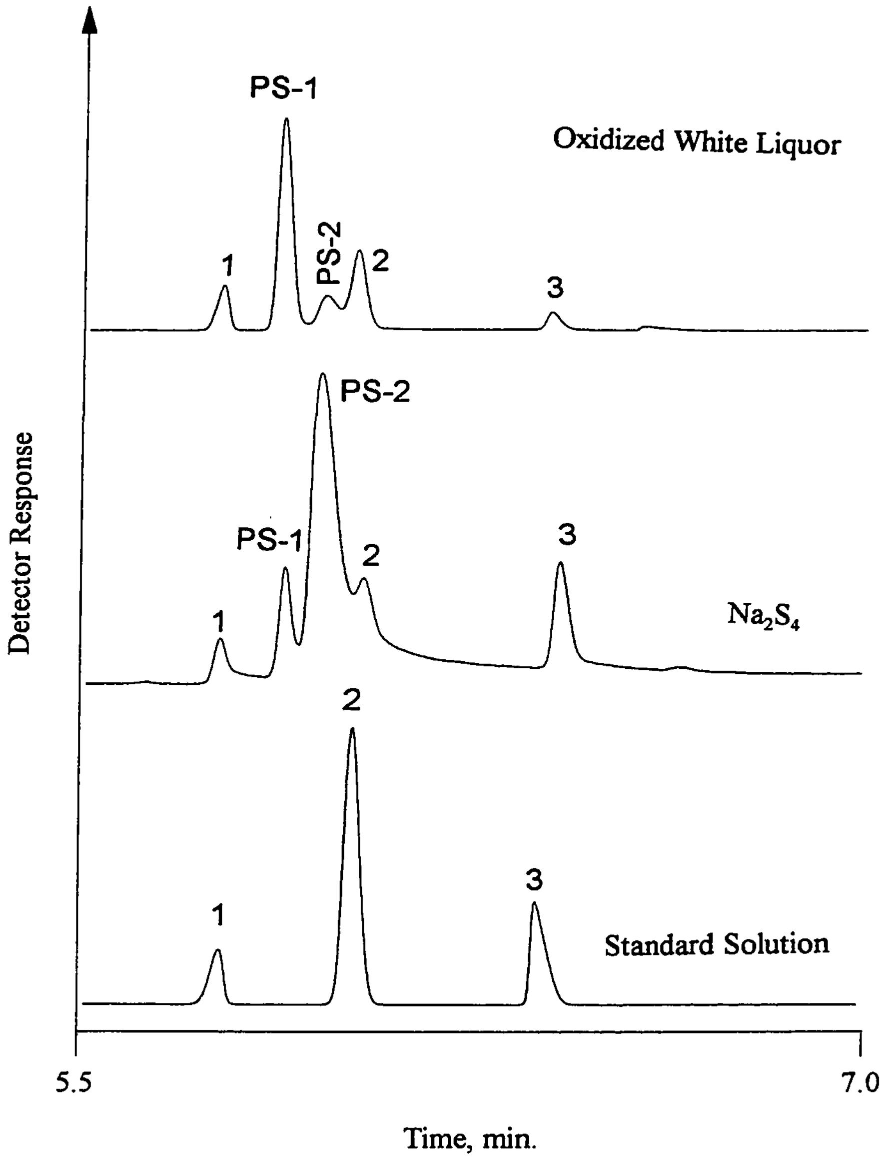

Figure 4.2. Separation of sulphur anions in: a standard mixture (lower trace); in a standard solution of sodium tetrasulphide (middle trace); and in a sample of oxidized white liquor (upper trace). Electrolyte as described in Figure 4.1. Peaks: thiosulphate (1), sulphide (2), sulphite (3) and polysulphide peaks PS-1 and PS-2. See text and Experimental for other conditions.

between 1.25 mM and 3 mM. As usual, a standard mixture containing sulphide, thiosulphate and sulphite was prepared in He-sparged water and analysed using the various electrolytes. The separations obtained with the three component standard are shown in Figure 4.3. As illustrated, the concentration of TTAOH had a significant impact on the migration time of thiosulphate. With 1.25 mM TTAOH in the electrolyte, all ions were well resolved and the order of migration was thiosulphate, sulphide and sulphite. The migration time and thus the mobility of thiosulphate decreased markedly as the concentration of TTAOH was increased. At a TTAOH concentration of 3 mM, thiosulphate eluted between sulphide and sulphite. These results clearly show that thiosulphate interacts strongly with TTAOH, significantly reducing the mobility of thiosulphate. This behaviour was observed previously using the chromate/TTAOH electrolyte. One possible mode of interaction of TTAOH with thiosulphate was postulated in Chapter 3 (cf. Figure 3.14). Subsequently, it was found that the ionic strength of the electrolyte could be increased marginally without sacrificing the resolution of the sulphur anions. For example, equivalent separations were obtained when 25 mM sodium sulphate/3.75 mM TTAOH and 20 mM/3 mM TTAOH were used. This result indicates that an increase in the sulphate concentration has the effect of reducing the interaction between TTAOH and thiosulphate.

4.3.4 Application of the Optimized Electrolyte to the Analysis of Tetrasulphide and Oxidized White Liquor

The suitability of using the 25 mM sodium sulphate/3.75 mM TTAOH electrolyte for the analysis of polysulphide in sodium tetrasulphide and oxidized white liquor samples was assessed by analysing a standard solution of the three sulphur anions (as described above),

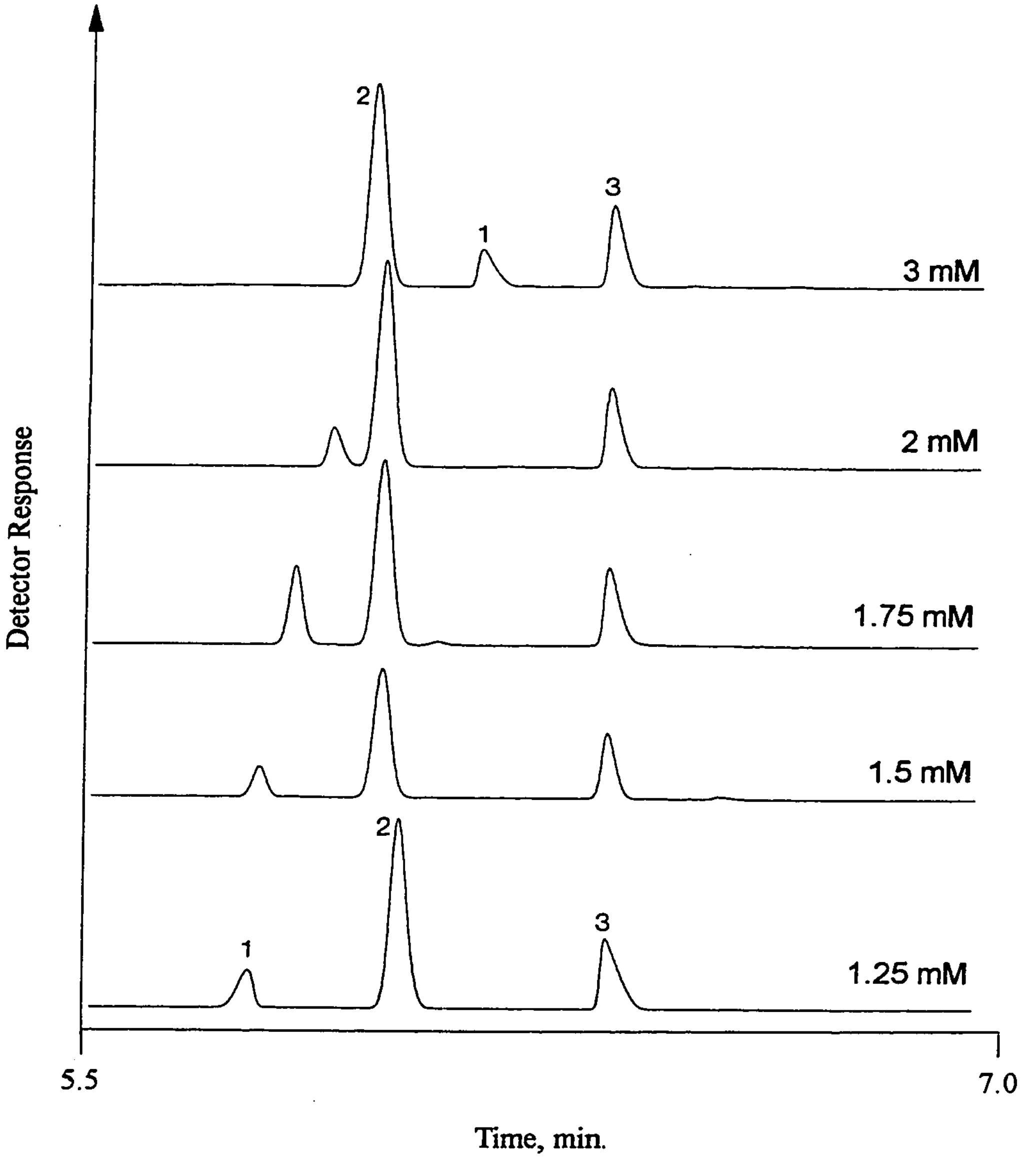

Figure 4.3. Effect of TTAOH concentration on the separation of thiosulphate (1), sulphide (2) and sulphite (3) in a standard mixture. The electrolyte was composed of 20 mM sodium sulphate with the indicated concentrations of TTAOH. See text and Experimental for other conditions.

along with a solution of commercially available sodium tetrasulphide and a sample of oxidized white liquor (known to contain polysulphide, PS). All solutions were prepared in He-sparged water and analysed immediately after dilution. As indicated in Figure 4.4, a much improved separation of the sulphur and polysulphide ions was obtained using the optimized electrolyte. As observed earlier, two polysulphide peaks (PS-1 and PS-2) can be seen in the electropherograms for the tetrasulphide and oxidized white liquor samples. As seen earlier, the oxidized white liquor sample has a higher ratio of PS-1 to PS-2 than does the tetrasulphide sample. If we assume that both PS-1 and PS-2 form a 1:1 complex with TTAOH, and since PS-1 migrates faster than PS-2, it follows that PS-1 must have a shorter chain length than PS-2. If these assumptions are correct, then oxidized white liquor contains more short chain PS than does sodium tetrasulphide. Moreover, PS-1 is probably comprised primarily of trisulphide, while the sodium tetrasulphide reagent is probably comprised largely of tetrasulphide, with a small amount of trisulphide.

4.3.5 Spectral Analysis of Sulphur Anions and Polysulphide-Bearing Samples Using Diode Array Detection

All CE analyses performed thus far were done with the crystal CE, which was equipped with a grating-based UV/Vis detector. To confirm the identity of the various peaks and to gain insight into the forms of polysulphide that may be present, subsequent CE analyses were conducted with the HP-CE instrument, which was equipped with a diode array detector. Analyses were first done on standard solutions containing the three sulphur anions, and then on samples of tetrasulphide and oxidized white liquor. The electrolyte used for the separations contained 25 mM sodium sulphate and 3.75 mM TTAOH. In addition, a bubble

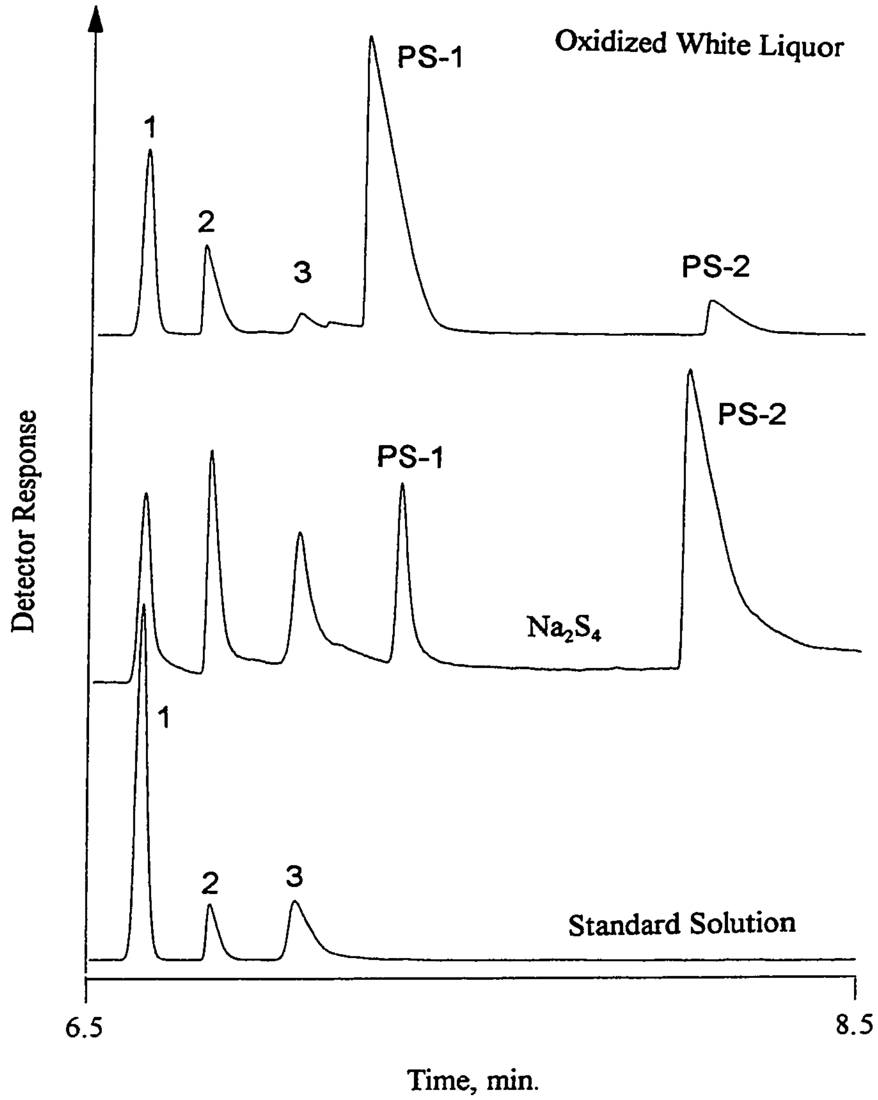

Figure 4.4. Separation of sulphur anions in a standard mixture, in sodium tetrasulphide and in oxidized white liquor. Peaks: Sulphide (1), thiosulphate (2) and sulphite (3), short chain polysulphide (PS-1) and long chain polsulphide (PS-2). See text and Experimental for other conditions.

capillary with a 50 μm i.d. (optical pathlength of 150 μm) was used instead of the 75 μm i.d capillary used previously. Figure 4.5 shows the spectra collected during the analysis of a standard mixture containing sulphide, thiosulphate, sulphite and hydroxide. As indicated, sulphide has a broad maximum centered near 230 nm, while thiosulphate has a maximum near 220. Sulphite has a maximum near 195 nm and hydroxide has no clear maximum, but rather absorbs significantly from 220 to 185 nm. Spectra collected for sulphide, thiosulphate and sulphite peaks during the analysis of sodium tetrasulphide and oxidized white liquor compare well with those obtained for a standard mixture, thus confirming the presence of these anions in the samples.

Spectra obtained for polysulphide peaks PS-1 and PS-2 during the analysis of the oxidized white liquor sample are shown in Figure 4.6. As indicated, the spectrum of PS-1 has a weak maximum centered near 295 nm and a more pronounced continuous absorption from 260 to 185 nm. The spectrum of PS-2 has a weak local maximum centered near 285 nm and a number of weak, poorly resolved absorption maximum between 260 and 185 nm. As indicated in Figure 4.7, spectra of the PS-1 peaks collected during the analysis of sodium tetrasulphide and oxidized white liquor are nearly identical. This indicates that both peaks are comprised of the same form of polysulphide. In addition, the spectra obtained for PS-1 and PS-2 are very similar to those obtained by Teder [5]. The evidence obtained from the CZE analyses indicate that at least two forms of polysulphide exist in oxidized white liquor and the major type of polysulphide appears to be the short chain version. In contrast, sodium tetrasulphide, which is listed as 90-95% pure, appears to be of lower purity, and in fact contains appreciable amounts of impurities such as sulphide, thiosulphate, sulphite.

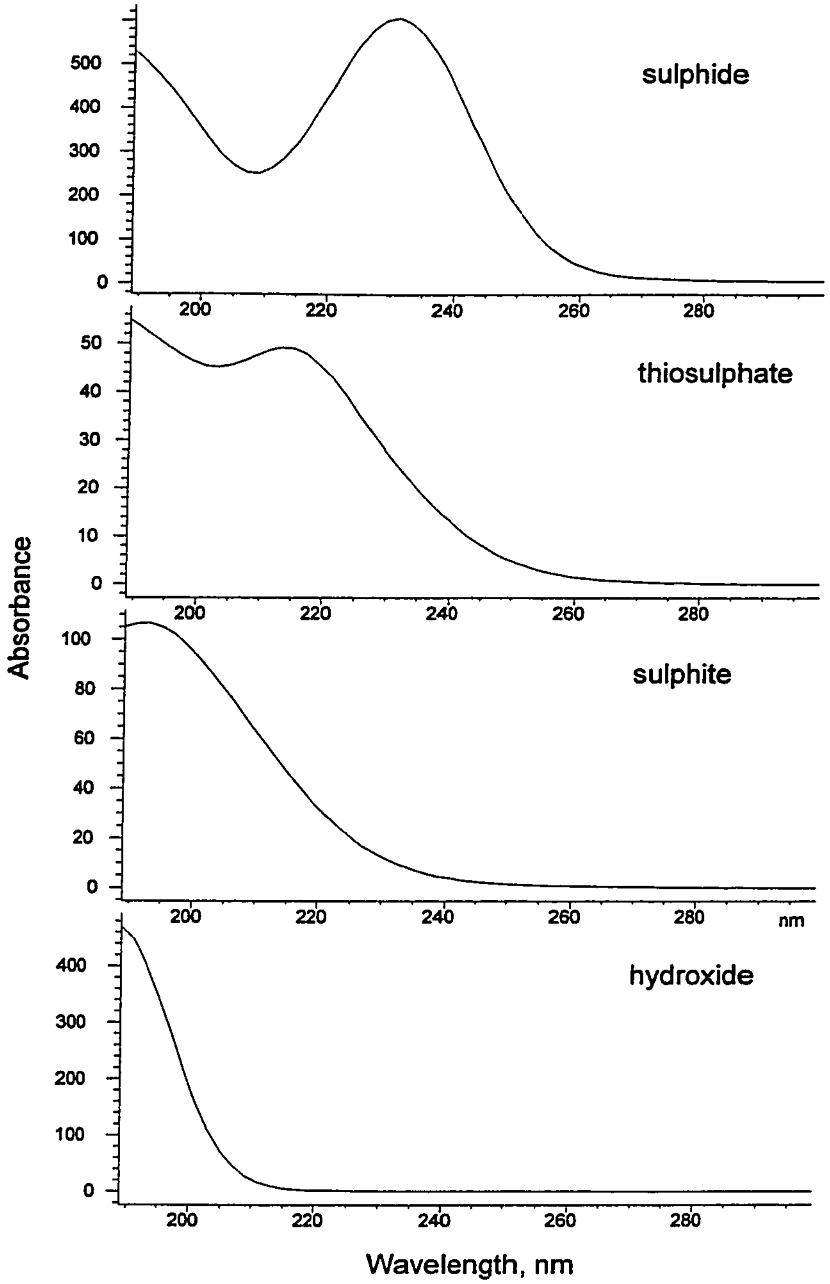

Figure 4.5. Spectra collected during the analysis of a standard mixture containing sulphide, thiosulphate, sulphite and hydroxide. See text and Experimental for other conditions.

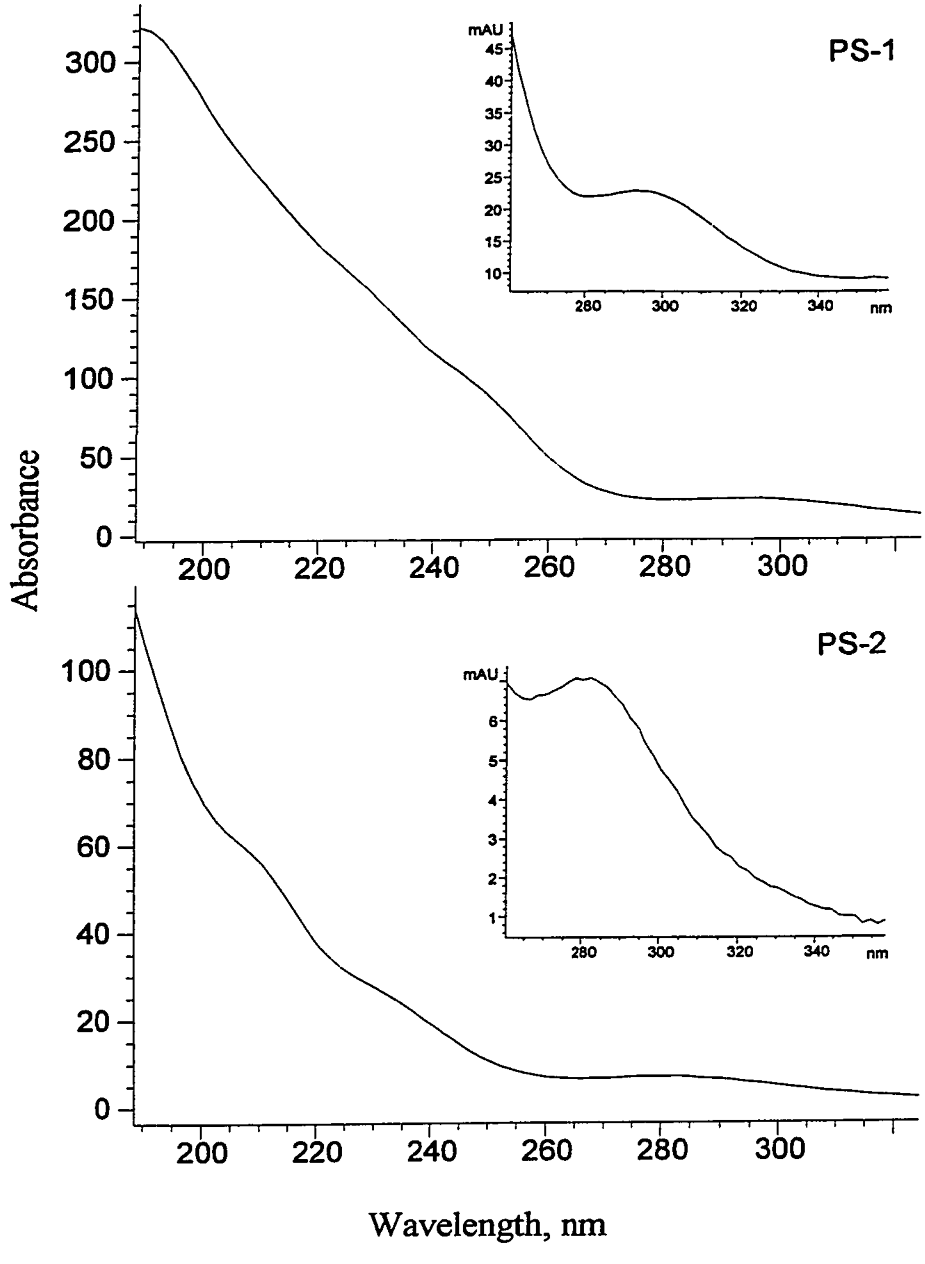

Figure 4.6. Spectra collected during the analysis of oxidized white liquor. The scanned peaks correspond to polysulphide peaks PS-1 and PS-2. See text and Experimental for other conditions.

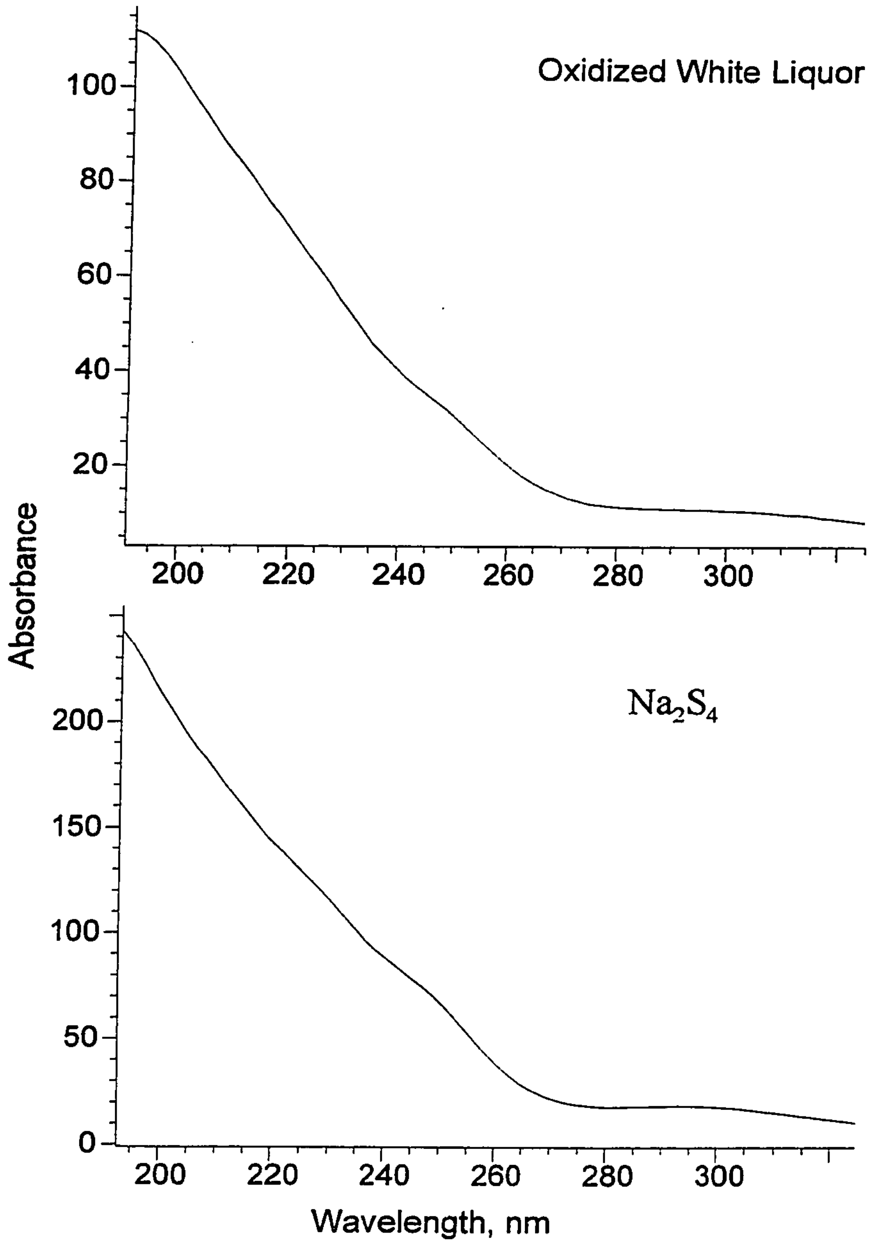

Figure 4.7. Comparison of the spectra obtained for the PS-1 peaks during the analysis of sodium tetrasulphide and oxidized white liquor. See text and Experimental for other conditions.

4.3.6 Quantitative Analysis of Sulphide, Thiosulphate and Hydroxide in White and Green Liquors

4.3.6.1 Linearity of Detector Response

Using the optimized electrolyte (25 mM sodium sulphate, 3.75 mM TTAOH), a series of anion standards covering the range of 2.5-50 mg/L (2.5-50 mM for NaOH) were prepared and analysed. Plots of peak area versus concentration for each anion were linear with correlation coefficients of 0.9998 or better, as indicated in Table 4.1.

Table 4.1. Linear regression results obtained from plots of peak area versus concentration over the range of 2.5-50 mg/L (2.5-50 mM for NaOH). Separations were done with a 25 mM chromate/3.75 mM TTAOH electrolyte. See text and Experimental for other conditions.

Anion	Intercept	Slope	Correlation Coefficient (R)
sulphide	0.075	2.316	0.9999
thiosulphate	-0.25	0.654	0.9998
sulphite	0.0027	1.279	0.9999
hydroxide	-0.41	7.690	0.9999

4.3.6.2 Repeatability of Migration Time and Peak Area for Standards

The repeatability of the migration time and of the peak area for a mixed standard containing 5 mg/L of each anion was determined by performing six replicate analyses. As shown in Table 4.2, the migration time and peak area RSD values were 0.2 and 0.3%, respectively.

4.3.6.3 Analysis of Hydroxide and Sulphide in Green and White Liquors

The accuracy of the CZE method for quantifying hydroxide (EA) and sulphide was

Table 4.2. Repeatability of migration time and peak area for a standard solution of sulphur anions and hydroxide. Each anion present at 5 mg/L. See text and Experimental for other conditions.

Anion	Migration Time (%RSD, n=6)	Peak Area (%RSD, n=6)
sulphide	0.2	0.3
thiosulphate	0.2	0.3
sulphite	0.2	0.3
hydroxide	0.2	0.3

evaluated by comparing the results obtained by CZE with those obtained by titrimetry (ABC titration). The samples were diluted 1:500 or 1:1000 in He-sparged water and analysed immediately by CZE and by titrimetry. As indicated in Table 4.3, the CZE and titrimetry results for each analyte are in excellent agreement.

Table 4.3. Comparison of hydroxide and sulphide results obtained by CZE and titrimetry (ABC) for samples of white and green liquor. See text and Experimental for other conditions.

Sample	[Analyte]			
	CZE [hydroxide] mM	Titrimetry [hydroxide] mM	CZE [sulphide] mg/L	Titrimetry [sulphide] mg/L
GL-1	1113	1082	11577	11780
WL-1	2838	2751	8931	8913

4.3.6.4 Recovery of Hydroxide, Thiosulphate and Sulphide from Green and White Liquors

The accuracy of the CZE method for the determination of hydroxide, thiosulphate and sulphide in green and white liquors, was assessed by performing spike-recovery experiments on each sample. Each samples was spiked with a single analyte, diluted to volume (1:1000) and then analysed immediately. As shown in Table 4.4, good recoveries of hydroxide and sulphide were obtained. The recovery of thiosulphate was high for both samples, possibly indicating that thiosulphate may be formed by the autoxidation of polysulphide.

Table 4.4. Recovery of hydroxide, sulphide and thiosulphate from green and white liquor samples. See text and Experimental for other conditions.

Anion	[Analyte], mg/L		Recovery (%)
	Added	Found	
GL-1			
hydroxide	1000	1020	102
thiosulphate	5000	5800	116
sulphide	10000	10300	103
WL-1			
hydroxide	3000	3120	104
thiosulphate	5000	5400	108
sulphide	9000	9180	102

4.3.6.5 Stability of Sulphur Anions and Polysulphide in White Liquor

An experiment was done to assess the stability of sulphur anions and polysulphide in dilute white liquor. The sample was diluted 1:1000 in He-sparged water and analysed within 5 minutes of preparation and a regular intervals thereafter. As shown in Table 4.5, sulphide was very stable, while thiosulphate and surprisingly polysulphide, were not affected significantly. In contrast, sulphite was very unstable. The instability of sulphite in polysulphide-containing samples was also observed in samples examined with the chromate electrolyte. In addition, sulphite was found to be unstable in a previous study [15]. A possible mechanism to explain the formation of sulphite from elemental sulphur was proposed earlier (cf. reaction 10 in Chapter 3).

Table 4.5. Stability of anions in dilute (1:250) white liquor. The sample was diluted in He-sparged water and analysed over the course of one hour. See text and Experimental for other conditions.

Time (min)	[Anion], mg/L			Polysulphide Peak Area (PS-1)
	sulphide	thiosulphate	sulphite	
5	8791	6350	592	34.07
23	8823	6585	884	33.42
42	8798	6794	1008	32.13
61	8769	6906	1106	30.88
mean	8795	6659	898	32.6
%RSD	**0.25**	**3.7**	**25**	**4.4**

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CHAPTER 5

SUMMARY AND SUGGESTIONS FOR FUTURE RESEARCH

Summary

From the results presented in Chapters 2-4 the following conclusions can be made:

1) Our evaluation of the suitability of a commercially available CE-based conductivity detector for the analysis of sulphide-bearing samples revealed that sulphide interacts strongly with the steel components in the cell, making the detector unsuitable for the analysis of sulphide. Furthermore, it was discovered that the cell components are susceptible to corrosion under relatively mild conditions, raising concerns about the long term viability and applicability of this detector.

2) This is the first work to unequivocally demonstrate that quinones participate in an oxygen-mediated redox reaction with sulphide in both model systems and in kraft black liquor to form thiosulphate and sulphite. It was discovered that glutathione (GSH), a biologically important thiol, can completely stabilize sulphide in the presence of model quinones and in black liquor. It is thought that GSH inhibits sulphide oxidation by scavenging free radicals as they are produced during quinone redox cycling.

3) Two new methods were developed for separating the major sulphur species present in kraft liquors. One employs indirect UV-detection and the second utilizes direct UV detection. The indirect method is suitable for determining the major sulphur anions, as well as hydroxide, carbonate, chloride, formate and oxalate in kraft liquors. The direct detection method is the

first reported CE method capable of determining a broad range of sulphur anions and hydroxide in kraft samples. Moreover, this is the first CE method developed for the speciation of inorganic polysulphide. The new methods should simplify the analysis of sulphur ions and hydroxide in kraft liquors.

Possibilities for future work

Based on the experimental results, the following recommendations for future work can be made:

1) The direct UV method could be refined and developed to allow for the quantitative analysis of polysulphide in kraft liquors. Further improvements in the electrolyte may be possible to allow for enhanced resolution of polysulphide from other anions. It may be possible to analyse much more concentrated samples by making a few simple changes to the electrolyte and analytical conditions used in the separation. In this way, solute rearrangement reactions, which often occur during sample dilution can be reduced.

2) The indirect method could be developed further to include the determination of carboxylic acids in kraft black liquors as well as the determination of oxychlorine species in chlorine dioxide bleach effluents. Methods could be also developed for analysis of alkali, alkaline earth and transition elements in pulp and paper mill process streams.