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### Effect of Sample-Related Sources of Error on the Analysis of Pulp and Paper Mill Process Liquids by Ion Chromatography: Part I—Determination of Sulphur Species

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EFFECT OF SAMPLE-RELATED SOURCES OF ERROR ON THE ANALYSIS OF  
PULP AND PAPER MILL PROCESS LIQUIDS BY ION CHROMATOGRAPHY:  
PART I - DETERMINATION OF SULPHUR SPECIES<sup>1</sup>

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ABSTRACT

Several factors which could affect the accuracy of measurements of sulphur species by ion chromatography have been identified. Analyses of sulphide, sulphite, sulphate and thiosulphate were conducted on samples of kraft liquors, spent sulphite liquor and newsprint white water. Erroneously high results were observed in the determination of sulphide in kraft white and green liquors, presumably due to shifts in equilibrium between elemental sulphur and polysulphide ions during sample dilution. Another problem was encountered during the analysis of sulphite in kraft liquors. Sulphite concentrations in diluted liquors rose rapidly with increase in time between dilution and injection into the ion chromatograph. Evidence presented in this paper suggests that, in diluted kraft liquors containing polysulphide and/or elemental sulphur, the sulphite concentration increases rapidly, possibly due to hydrolysis of elemental sulphur. Determination of thiosulphate was also subject to positive errors, due to oxidation of sulphide to thiosulphate. The effect of storage conditions on the stability of sulphur species was also determined. Room-temperature storage was the most deleterious for white water samples containing low levels of sulphur ions. Long-term stability in all samples was much improved by refrigeration or freezing. Kraft liquors were very stable even when stored at room temperature. Various recommendations are made to maintain sample integrity and minimize analysis errors.

### INTRODUCTION

Ion chromatography (IC) has become a widely accepted technique for the determination of a variety of inorganic anions. Over the past few years, it has gained increased popularity in the pulp and paper industry where it is mainly used for the determination of sulphur and chlorine species in process liquids and effluents<sup>2</sup>. Several papers deal with specific applications such as the determination of various anions in kraft black liquor<sup>3</sup>, sulphate in green<sup>4</sup> and black<sup>5</sup> liquors, total sulphur and chlorine in pulps and liquors<sup>6</sup>, as well as thiosulphate and other ionic species in newsprint mill process waters<sup>7-9</sup>.

Although the chromatographic conditions for these analyses, such as the type of column, eluent, and detector, are all based on well-established procedures developed on standard samples, little work has been reported on assessing the accuracy and reliability of the results for various types of process liquors. Some progress toward method evaluation and validation has been made by Easty *et al.*<sup>10,11</sup>. However, their work was largely confined to black liquors and may not be applicable to other types of samples. For example, we found that the IC analyses of sulphide were generally in poor agreement with the results obtained by a conventional titrimetric method, particularly in the case of strongly alkaline samples, such as kraft white and green liquors. In addition, analyses of sulphite in kraft liquors showed an unusually high degree of scatter which could not be attributed to conversion of sulphite to sulphate, since the samples were preserved to prevent oxidation. Erroneous results can also be obtained for mill samples that are not analyzed shortly after collection. In many cases, an ion chromatograph is not available at the mill site, and consequently, samples must be shipped to a central laboratory or to other outside facilities for analysis. Further delays can be incurred at the testing laboratory. Thus, it can take sometimes 2-3 weeks, possibly longer, from the time a sample is collected until it is analyzed. During this period, changes in concentrations of sulphur or chlorine ions due to

oxidation or decomposition could make the results meaningless. For example, Butterfield and Glogowski<sup>12</sup> have reported a 60% decrease in thiosulphate concentration of a simulated white water sample after three days of storage. To our knowledge, however, the effect of storage time and temperature on the stability of these ions has not been fully documented.

In the light of the foregoing remarks, we set out to examine some of the problems encountered during the IC analysis of various types of process liquors, and to determine the effect of storage conditions on the accuracy of IC measurements. In Part I of this investigation, analyses of sulphide, sulphite, sulphate and thiosulphate were conducted on samples of kraft white, green and black liquors, spent sulphite liquor and newsprint white waters. Part II will deal with the analysis of chlorine species in bleaching liquors.

#### EXPERIMENTAL

The experimental program for this work consisted of two phases. In Phase I, we assessed the accuracy of measurements of sulphur species and, in Phase II, we examined the stability of these species under various storage conditions.

Only general sampling and chromatographic conditions are described in this section. Specific details concerning the type and treatment of samples are presented separately for each ion under "Results and Discussion".

#### Collection and Storage of Samples

For Phase I of this study, samples were collected, in plastic containers, from several kraft and newsprint mills and were refrigerated at 5°C. All samples were allowed to reach room temperature before they were analysed.

In Phase II, an elaborate sampling scheme was devised for determining the stability of sulphur species under various storage conditions. Samples of kraft white and black liquors, spent acid

sulphite liquor and newsprint white water were collected in plastic containers at mill sites, brought back the same day to our laboratory and were immediately refrigerated overnight. The kraft liquors were collected from a hardwood mill. The spent sulphite and white water were obtained from a newsprint mill which used a furnish consisting of 42% ultra-high yield (90%) acid sulphite and 58% sodium hydrosulphite bleached groundwood. All four samples were analyzed the following day, denoted as "Day 0". After this initial analysis, each sample was split into three portions, and each portion was divided into 6-60 mL plastic bottles. One of the 6-bottle set was stored at room temperature (23°C), the second was refrigerated (5°C), and the third was frozen (-15°C). Bottles were then withdrawn at weekly intervals, allowed to reach room temperature, and then analyzed by ion chromatography.

#### Ion Chromatography

Analyses were performed on a Dionex Model 4000i ion chromatograph equipped with conductivity and UV detectors. Sulphide determinations were also conducted on a Dionex Model 2010i ion chromatograph equipped with an electrochemical detector. Chromatographic conditions were essentially based on those described by the manufacturer and later applied by Easty *et al.*<sup>10,11</sup>, and are described below:

#### Sulphide:

Column: Dionex AS3 with AG3 guard column  
Eluent: 1 mM Na<sub>2</sub>CO<sub>3</sub>, 10 mM each of NaOH and H<sub>3</sub>BO<sub>3</sub>, 15 mM ethylenediamine (EDA)  
Flow rate: 2 mL/min  
Detector: UV (215 nm) or electrochemical (EC)  
Diluent: Water

For white and green liquor analyses, both eluent and diluent were adjusted to pH 13 with NaOH.

To prevent oxidation of sulphide, eluent and diluent were both fully degassed by vacuum aspiration for 30 min. A sulphide

antioxidant buffer (SAOB), consisting of 17.6 g ascorbic acid, 8 g 50% NaOH, and 1.0 mL EDA in 100 mL of degassed, deionized water, was also added as 1 mL/L to diluted samples. In the case of white and green liquor analyses with EC detection, addition of EDA to the eluent and SAOB to the diluent were omitted because, at a pH of 13, EDA gave a response which interfered with the sulphide analysis.

#### Sulphite and Sulphate

Column: Dionex AS4 with AG4 guard column  
Eluent: 2.25 mM Na<sub>2</sub>CO<sub>3</sub> and 2.8 mM NaHCO<sub>3</sub>  
Flow rate: 1.5 mL/min  
Detector: Conductivity  
Suppressor: Anion micromembrane (AMMS)  
Diluent: 1% isopropanol in water

Stock sodium sulphite solutions, each containing 1000 mg/L of sulphite (as SO<sub>3</sub><sup>2-</sup>), were prepared in a 10% isopropanol solution in water. Addition of isopropanol to both stock solution and diluent was necessary to prevent oxidation of sulphite to sulphate.

It should be noted that, although the AS4 column was used in this work, other types of columns, such as the AS3, could also be used. The major difference between the AS3 and AS4 columns is a larger particle size of the packing material in the former (25 µm, compared with 15 µm for the AS4 resin), giving rise to longer retention times. We did not experience plugging problems with the AS4 column during analysis of spent pulping liquors, as reported by Easty *et al.*<sup>10</sup>. The AS4A column is not recommended for complex samples, such as black liquors, because it gives a poor resolution of sulphite and sulphate (~1 min), whereas the AS4 column provides a separation of about 4 minutes between peaks. This better resolution is probably due to the considerably higher degree of crosslinking of the AS4 resin (3.5%) compared with that of the AS4A (0.5%).

#### Thiosulphate

Column: Dionex AG4 with NG1 guard column

Eluent: 2.25 mM Na<sub>2</sub>CO<sub>3</sub>, 2.8 mM NaHCO<sub>3</sub>, 0.8 mM p-cyanophenol and  
2% acetonitrile  
Flow rate: 2 mL/min  
Detector: Conductivity  
Suppressor: Anion micromembrane (AMMS)  
Diluent: Water

The mobile phase (MPIC) NG1 guard column was used instead of a second AG4 column because it does not contain ion-exchange sites and, consequently, the thiosulphate retention time is not increased.

### RESULTS AND DISCUSSION

#### I. DETERMINATION OF SULPHUR SPECIES IN VARIOUS TYPES OF PROCESS LIQUORS

##### 1. Determination of Sulphide

Sulphide determinations were confined to kraft mill samples, including white, green and black liquors. Both UV and EC detectors were used in this study and the results were compared with those obtained by potentiometric titration with mercuric chloride using a sulphide ion-selective electrode in accordance with the method of Papp<sup>13</sup>.

##### Black Liquors

Black liquors were diluted with deionized, degassed water containing 1 mL/L SAOB. Other diluents were tried, including using eluent as diluent, but the results obtained were found to be in poor agreement with the potentiometric method. Measurements were carried out on six weak and two strong black liquors using either the UV or EC detector. Liquors were diluted to a concentration range between 2.5 to 10 ppm for UV detection and 1.0 to 2.5 ppm for electrochemical detection.

Generally good agreement was found between the IC methods and the potentiometric method (Table I). Small differences between the two sets of data are likely due to the fact that the liquors were not measured by the two methods at the same time and, consequently, some oxidation may have occurred.

TABLE 1. Concentrations of Sulphide in Black Liquors as Determined by Ion Chromatography and by Potentiometry.

Sample	Set 1		Set 2	
	IC (UV Detection)	Potentiometry	IC (EC Detection)	Potentiometry
	g/L (as S <sup>2-</sup> )		g/L (as S <sup>2-</sup> )	
Weak black liquors				
1	2.46	2.85	3.30	3.52
2	3.49	3.48	3.46	3.36
3	6.95	6.96	6.58	6.66
4	6.70	6.43	6.36	6.19
5	5.10	5.17	4.78	4.81
6	4.67	4.75	4.24	4.61
Strong black liquors				
1	10.5	10.4	8.26	8.01
2	12.8	13.3	14.1	14.4

The results show that either UV or EC detection can be used for sulphide measurements. However, the UV detector offers the advantage of allowing for measurements to be made over a higher and wider concentration range than the EC detector, as reported by Easty and Johnson<sup>11</sup>. Thus, less sample dilution is required and sulphide oxidation is reduced. On the other hand, higher dilution levels are required with the EC detector to prevent fouling of the silver electrode. We found, however, that it was desirable to use higher sulphide concentrations than those recommended by the manufacturer. Although this may require more frequent cleaning of the electrode, it reduces the rate of sulphide oxidation in the diluted sample.

We also determined the recovery of sulphide from an oxidized black liquor sample containing no sulphide ions. The liquor was spiked with known amounts of sulphide and the sulphide concentration was measured using UV detection. As indicated in Table II, the percent recovery ranged between 99-101% confirming the reliability of the method.

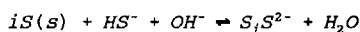


Table 2. Recovery of Sulphide from Spiked Oxidized Black Liquor

Concentration of Sulphide Standard mg/L (as S <sup>2-</sup> )		
Added	Recovered	% Recovery
2500	2475	99
5000	5050	101
7500	7575	101

#### White and Green Liquors

Analysis of sulphide in white and green liquors, using a simple dilution technique as outlined for black liquors, produced results that were considerably higher than those obtained by the potentiometric method (Table III). This was attributed to the fact that the high levels of dilution typically required for these liquors (2500x) resulted in a decrease in pH from about 13 to 11. This can, in turn, produce changes in the equilibrium concentrations between elemental sulphur, polysulphide and sulphide; all of which are present in white and green liquors. According to Teder<sup>14</sup>, in an aqueous polysulphide solution in equilibrium with elemental sulphur, the concentration of HS<sup>-</sup> ions increases inversely with the alkalinity. He proposed that the equilibrium between elemental sulphur (iS) and polysulphide ions (S<sub>i</sub>S<sup>2-</sup>) of different size can be written as:



It can therefore be postulated that as a sample is diluted, the alkalinity decreases and the equilibrium shifts to the left resulting in the formation of HS<sup>-</sup>. At the high pH used in this work, essentially all the HS<sup>-</sup> would be converted to S<sup>2-</sup>.

TABLE 3. Concentrations of Sulphide in White and Green Liquors as Determined by Ion Chromatography (pH 11) with UV Detection\* and by Potentiometry.

Sample	IC	Potentiometry
	g/L (as S <sup>2-</sup> )	
White liquors		
1	17.9	15.2
2	18.3	15.1
3	16.2	13.7
4	17.2	15.5
Green liquor	13.3	12.2

\* In this work, a wavelength of 230 nm was used instead of 215 nm. However, this had no significant effect on the results.

To confirm this hypothesis, further experiments were conducted by diluting the sample in eluent previously adjusted to pH 13. The sulphide results obtained on these pH adjusted samples were in close agreement with the potentiometric method (Table IV). It is therefore recommended, for measurements of sulphide in white and green liquors, to adjust the pH of the diluted sample and eluent to that of the original liquor (approx. pH 13) to avoid shifts in equilibrium between elemental sulphur and polysulphide ions.

#### Stability of Standard Sulphide Solutions

The stability of both stock and dilute standard sulphide solutions were determined. A 1 g/L stock sulphide solution was prepared using degassed, deionized water and adjusted to pH 13. The sulphide concentration was measured daily by potentiometric titration and was found to decrease steadily from 1.054 mg/L to 0.942 (11%) over a 4-day period. An even more pronounced decrease (17%) over the same time period was found for a stock solution prepared in 50% SAOB as recommended by Easty *et al.*<sup>10</sup>. This emphasizes the importance of measuring the concentration of the

TABLE 4. Concentrations of Sulphide in White and Green Liquors (pH 13) as Determined by Ion Chromatography with UV Detection and by Potentiometry.

Sample	IC	Potentiometry
	g/L (as S <sup>2-</sup> )	
White liquors		
1	14.5	15.2
2	16.0	15.1
3	13.3	13.7
4	16.0	15.5
5	15.9	15.9
Green liquors		
1	10.6	11.4
2	16.1	16.0
3	12.5	12.4

stock sulphide solution, by potentiometry or other means, on the same day that a particular analysis is performed.

Dilute solutions containing 2.5, 5.0 and 10 mg/L of sulphide were prepared in degassed, deionized water containing 1 mL/L of SAOB. Several measurements were made, using UV detection, over a period of approximately 40 min from the time of dilution until the peak was eluted. A decrease in peak height of 6, 3 and 2% was observed over this time for 2.5, 5.0 and 10 mg/L solutions, respectively. This indicates that both standards and samples should be analyzed immediately after dilution to prevent losses of sulphide.

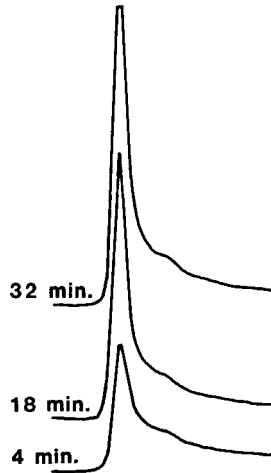
It should also be pointed out that several injections of a concentrated sulphide solution (25 mg/L) are required prior to analysis in order to condition the column. If an EC detector is used, the column should be first disconnected from the detector prior to injection of the concentrated sulphide solution in order to avoid fouling of the silver electrode. This treatment is followed by repeated injections of dilute standard until at least three reproducible peaks are obtained. The calibration curve should

include three to four points covering the range of concentration used.

## 2. Determination of Sulphite and Sulphate

One of the problems with sulphite analysis is that it can readily undergo oxidation to sulphate. Formaldehyde has long been recognized as an effective sulphite stabilizer and is commonly used for this purpose e.g.,<sup>9</sup>. However, the major drawback associated with it is that both peak height and retention time of sulphite vary significantly with the amount of formaldehyde added<sup>11,15</sup>. Therefore, for accurate results, it is essential to use the same molar ratio of sulphite to formaldehyde in both standard and sample, which is not practical and subject to errors. Accordingly, we investigated the possibility of using an alternate oxidation inhibitor. Lindgren and Cedergren<sup>15</sup> evaluated several potential sulphite stabilizers, including various alcohols, such as isopropanol, and saccharides. Although somewhat less effective than formaldehyde, particularly for long-term stabilization (>24 h), they do not suffer from the same drawback as formaldehyde. Isopropanol was selected for our work. A 2.5 mg/L sulphite standard containing 1% isopropanol was analyzed immediately after dilution and three hours later. The peak height decreased by only 4% during this period and there was no change in retention time compared with an unstabilized sample.

A more serious problem related to sulphite stability was encountered during analysis of kraft liquors. Sulphite analyses on black and white liquors showed a high degree of scatter. This could not be attributed to sulphite oxidation since the samples had been stabilized with isopropanol and, moreover, this problem was not observed with liquors from other processes, such as spent sulphite or newsprint white water. We discovered that, with kraft liquors, the sulphite concentration rose rapidly with increase in time between sample dilution and injection. In addition, the sulphite peak showed pronounced tailing. Figure 1 shows this phenomenon for a kraft mill white liquor sample. Within a 30 min period after sample dilution, the peak height increased by about 3 fold.



**FIGURE 1:** Superimposed chromatograms of sulphite in a kraft mill white liquor sample. The time between sample dilution and injection is indicated for each peak.

Surprisingly, this effect was not observed with fresh white liquors prepared in our pilot plant. The sulphite peak was symmetrical and its height remained practically constant up to about 30 min after sample dilution (Figure 2). The major difference between mill and pilot plant samples is the presence of significantly higher levels of polysulphide and/or elemental sulphur in the former. The pilot plant sample was colorless, indicating a relatively low level of polysulphide and/or elemental sulphur. Therefore, we suggest that sulphite instability in diluted kraft liquors may be due to the presence of polysulphide and/or elemental sulphur which is only present in mill liquors but not in the pilot plant sample to any significant extent. To test this hypothesis, a pilot plant white liquor sample was analyzed before and after addition of sulphur to produce polysulphide. As indicated in Figure 3, the liquor containing sulphur exhibited similar behavior to the mill sample, with the sulphite concentration increasing rapidly over a one hour period from dilution. However, in the untreated liquor, the

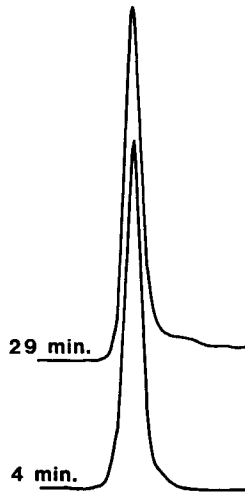


FIGURE 2: Superimposed chromatograms of sulphite in a pilot plant white liquor sample. The time between sample dilution and injection is indicated for each peak.

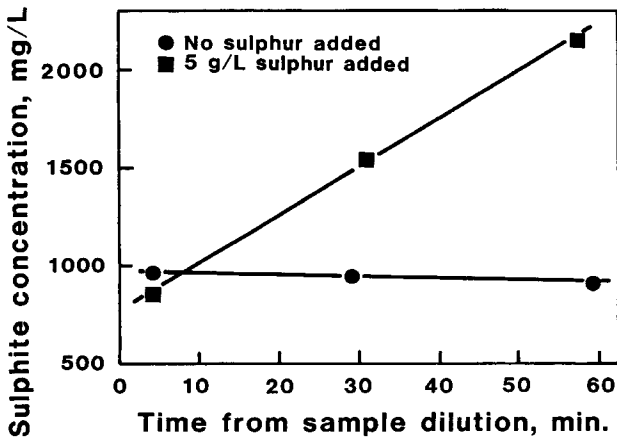
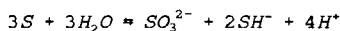


FIGURE 3: Sulphite concentration in a pilot plant white liquor sample, measured at various times after sample dilution, before and after addition of sulphur.

sulphite concentration remained essentially constant over the same time period.

It was apparent, therefore, that in dilute kraft mill liquors, the presence of polysulphide and/or elemental sulphur promotes the rapid formation of sulphite. A possible explanation for this effect is that, once the sample is diluted, the alkalinity decreases and this results in precipitation of elemental sulphur, as described by Teder<sup>14</sup>. In the presence of dilution water, the precipitated sulphur could then produce sulphite according to the following reaction<sup>16</sup>.



It appears, however, that if the sample is promptly injected into the IC, there is no significant conversion to sulphite, as evidenced by the initial level of sulphite in Figure 3 which is about the same in both treated and untreated samples. Accordingly, for sulphite determinations in kraft liquors, the sample must be analyzed immediately after dilution to minimize this effect. It is still likely, however, that this precaution may not eliminate the problem in all cases. Other means of minimizing sulphite formation in diluted samples are presently under investigation.

In contrast to sulphite analysis, sulphate determination was relatively straightforward. Concentrations of sulphate in diluted samples, including kraft liquors, were relatively stable. This is also in agreement with the results of Easty and Johnson<sup>10</sup> who reported that sulphate in green liquor was stable up to at least a half hour after dilution, provided that deoxygenated water was used for dilution.

Tables V and VI show the recovery of sulphite and sulphate, respectively, from spiked samples. The percent recovery was excellent in all cases, which confirms that, if the sample is immediately injected after dilution, there is no significant increase in sulphite concentration.

### 3. Determination of Thiosulphate

Analysis of thiosulphate with the ion-exchange columns commonly used for other sulphur species (e.g., AS3 or AS4) produced long

TABLE 5. Recovery of Sulphite from Spiked Samples.

Sample	Initial Concentration mg/L (as SO <sub>3</sub> <sup>2-</sup> )	Concentration of Sulphite Standard mg/L (as SO <sub>3</sub> <sup>2-</sup> )		
		Added	Recovered	% Recovery
Strong black liquor*	3.7	7.7	7.6	99
Weak black liquor	563	200	197	98
Green liquor	2402	4120	3980	97
Newsprint white waters				
1	Not detected	1640	1680	102
2	334	414	415	100
3	149	414	420	101
4	1173	1650	1680	102

\* For the strong black liquor sample, the results are expressed in mg/g.

TABLE 6. Recovery of Sulphate from Spiked Samples.

Sample	Initial Concentration mg/L (as SO <sub>4</sub> <sup>2-</sup> )	Concentration of Sulphate Standard mg/L (as SO <sub>4</sub> <sup>2-</sup> )		
		Added	Recovered	% Recovery
Strong black liquor*	21.8	15.0	15.0	100
Weak black liquor	3140	500	497	99
Green liquor	3410	2000	1930	96
Newsprint white waters				
1	482	400	393	98
2	100	200	201	100
3	851	800	772	96

\* For the strong black liquor sample, the results are expressed in mg/g.



retention times, peak tailing and reduced sensitivity. This is due to the fact that the  $S_2O_3^{2-}$  ion has a strong affinity for the stationary phase and therefore is more strongly adsorbed on the column. Stronger eluents are required and consequently, the background conductivity is more difficult to suppress.

To improve the separation of hydrophobic anions, such as thiosulphate, a new stationary phase, referred to as AS5, was recently introduced by Dionex. Use of this column, together with addition of p-cyanophenol to the eluent to minimize  $S_2O_3^{2-}$  adsorption, was claimed to give satisfactory results. However, we found that equally good separation can be obtained with the conventional AS4 or AS4A column and by using a standard  $CO_3^{2-}/HCO_3^-$  eluent, provided that p-cyanophenol is added to the eluent. A further substantial reduction in retention time can be achieved by using an AG4 column which is a shorter version of the AS4 and normally serves as a guard column. This is illustrated in Figure 4, which shows 3 superimposed  $S_2O_3^{2-}$  chromatograms recorded under different conditions.

The retention time was decreased from 23 min in peak 1 to about 5 min in peak 3. A considerable improvement in peak shape and sensitivity was also observed. Accordingly, the AG4 guard column was adopted for routine determination of thiosulphate. Although this combination of short column and stronger eluent produced a much improved thiosulphate separation, it also resulted in coelution of other ions, including chloride, sulphite and sulphate. Separation of all these ions including thiosulphate, in a single run, can probably be best achieved with gradient elution.

A potential problem with thiosulphate analysis occurs with samples containing high levels of sulphide, such as kraft liquors. In diluted samples, sulphide oxidizes to thiosulphate, resulting in an increase in thiosulphate concentration.

Since the sulphide antioxidant buffer (SAOB) is not compatible with the conductivity detector<sup>10</sup>, it cannot be used to stabilize sulphide during thiosulphate analysis. To determine the extent of this oxidation problem, we measured thiosulphate concentration in

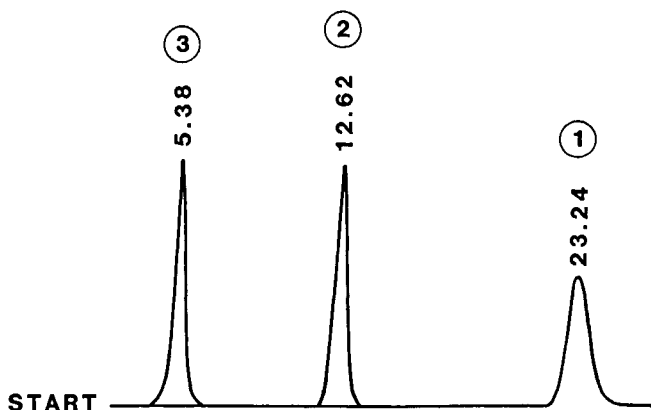


FIGURE 4: Superimposed chromatograms of thiosulphate. Chromatograms 1 and 2 were obtained with an AS4A column, and chromatogram 3 with an AG4 guard column. For chromatograms 2 and 3 only, p-cyanophenol was added to the eluent. The retention time is indicated above each peak.

white and black liquor samples at several time intervals after sample dilution. As indicated in Figure 5, the stability in white liquor was considerably greater than in black liquor. Over a one hour period after dilution, the thiosulphate increased by about 30% in black liquor and by only 4% in the white liquor. The reason for this large difference between the two types of liquor is not clear at the moment. However, these results show that, at least for black liquor samples, thiosulphate analysis should be performed immediately after sample dilution.

The accuracy of the IC technique for measuring thiosulphate was assessed by comparing results on three black liquor samples with those obtained by polarography. Polarographic techniques are considered to be far more reliable and sensitive than titrimetric methods for measuring thiosulphate, and consequently have been widely adopted for this purpose<sup>12,17,18</sup>. As indicated in Table VII, good agreement was observed with the IC technique; the difference between the means was only 2%.

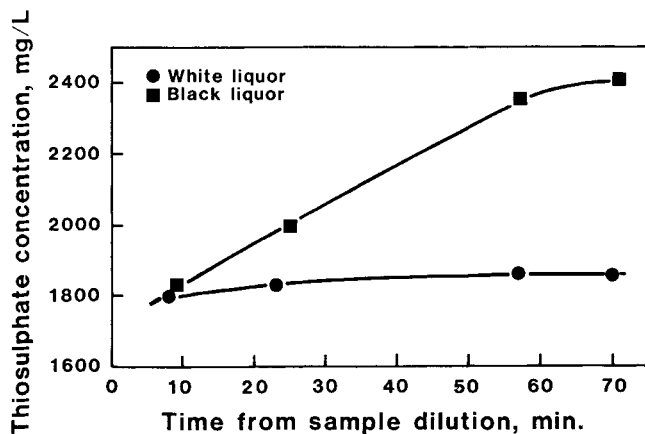


FIGURE 5: Variation in thiosulphate concentration in white and black liquors with length of time after sample dilution.

TABLE 7. Concentrations of Thiosulphate in Black Liquors as Determined by Ion Chromatography and Polarography.

Sample	Ion Chromatography	Polarography
	g/L (as $S_2O_3^{2-}$ )	
1	3.87	3.76
2	4.45	4.27
3	3.86	3.91
Mean	4.06	3.98

We also determined the percent recovery of thiosulphate from spiked samples (Table VIII). The recovery ranged between 94-105% with an average of 99%.

## II. STABILITY OF SULPHUR SPECIES UNDER VARIOUS STORAGE CONDITIONS

### Kraft Black and White Liquors

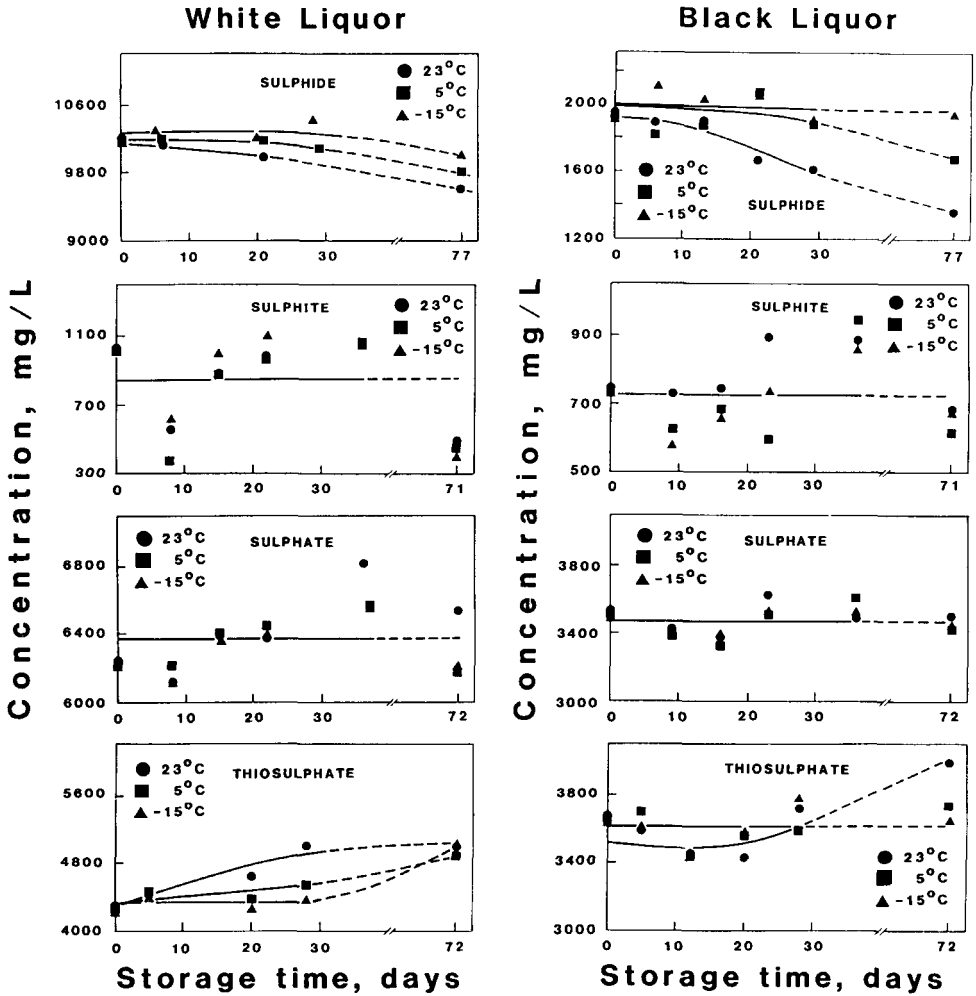
The effect of storage time and temperature on the concentration of all 4 sulphur ions is shown in Figures 6 and 7 for white and

TABLE 8. Recovery of Thiosulphate from Spiked Samples.

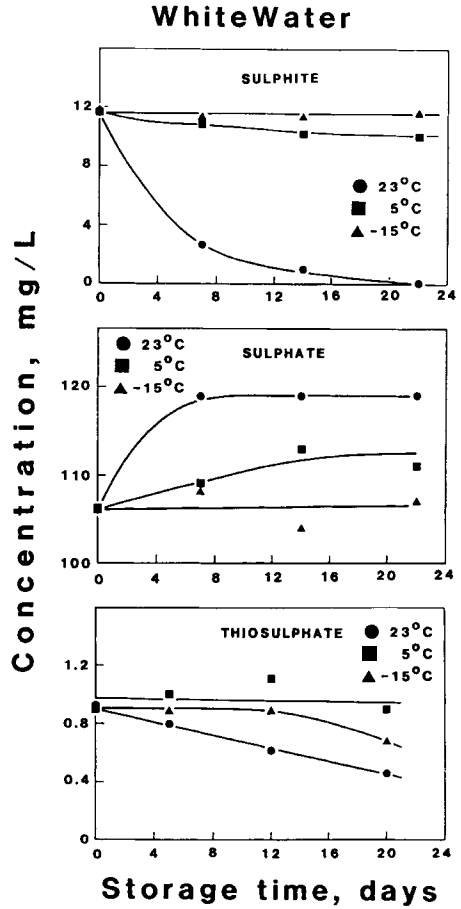
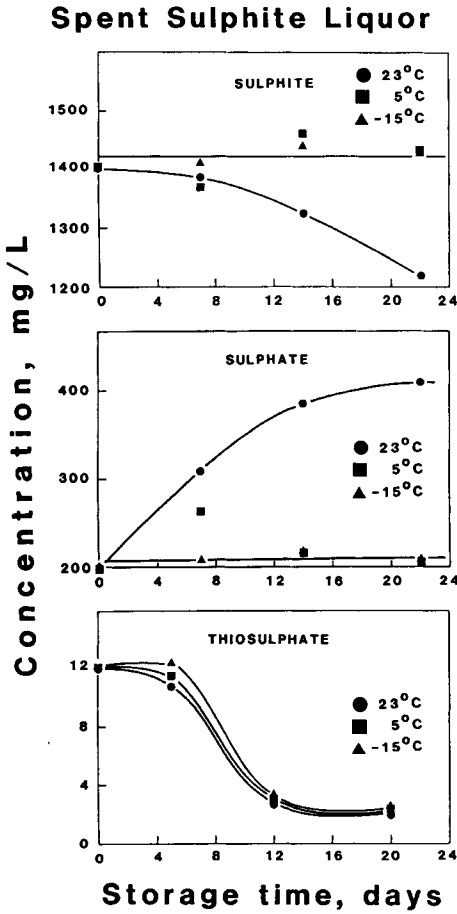
Sample	Initial Concentration mg/L (as $S_2O_3^{2-}$ )	Concentration of Thiosulphate Standard mg/L (as $S_2O_3^{2-}$ )		% Recovery
		Added	Recovered	
Black liquor	3681	2260	2130	94
Green liquor	4518			
addition 1		4530	4430	98
addition 2		9070	8570	94
Newsprint white water	16.6			
addition 1		22.6	23.7	105
addition 2		45.2	46.6	103

black liquors, respectively. For samples stored at 5 and  $-15^{\circ}\text{C}$ , the concentrations of  $S^{2-}$ ,  $SO_4^{2-}$  and  $S_2O_3^{2-}$  were essentially constant after about 30 days. At room temperature ( $23^{\circ}\text{C}$ ), some changes in  $S^{2-}$  and  $S_2O_3^{2-}$  concentrations were observed, particularly in the black liquor sample, but only after 3 weeks of storage. More significant changes in  $S^{2-}$  and  $S_2O_3^{2-}$  concentrations occurred at longer storage time. After 77 days, the  $S^{2-}$  concentration decreased by 30% and  $S_2O_3^{2-}$  increased by 9%, probably mainly due to  $S^{2-}$  oxidation. Changes were considerably less pronounced for samples stored at 5 and  $-15^{\circ}\text{C}$ . The  $SO_4^{2-}$  concentration, on the other hand, remained practically unchanged in both white and black liquors even at the longest storage time (72 days). The small percentage variation between data points was largely due to experimental scatter.

In the case of sulphite analysis, there was no apparent trend toward changes in concentration during storage; however, with both liquors the data showed a considerable degree of scatter, as reported previously, making it difficult to draw any meaningful conclusions. In the white liquor sample, the measured sulphite concentration ranged from 370 to 1100 mg/L, and, in black liquor, from 570 to 970 mg/L! It should be noted, however, that these measurements were performed prior to discovering the high



FIGURES 6 & 7: Effect of storage time and temperature on the concentration of sulphide, sulphite, sulphate and thiosulphate in kraft white (Fig. 6) and black (Fig. 7) liquors.



FIGURES 8 & 9: Effect of storage time and temperature on the concentration of sulphite, sulphate and thiosulphate in spent acid sulphite liquor (Fig. 8) and newsprint white water (Fig. 9).

instability of sulphite in diluted samples. It is likely, therefore, that the analyses were not performed immediately after dilution, resulting in widely scattered results.

#### Spent Acid Sulphite Liquor and Newsprint White Water

The concentrations of  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  as a function of storage time and at each of the 3 storage temperatures are shown in Figures 8 and 9 for the spent acid sulphite liquor and newsprint white water, respectively. Sulphide was not measured in these samples since it was not expected to be present in any significant concentration. In both cases, storage at room temperature ( $23^\circ\text{C}$ ) produced significant changes in the concentration of all three ions even after a relatively short storage time. In white water, for example,  $\text{SO}_3^{2-}$  decreased by 78% after 5 days of storage due to oxidation to sulphate. In both types of samples, a decrease in sulphite concentration was accompanied by an increase in sulphate concentration. The stability of all three sulphur ions was much improved after storage at 5 or  $-15^\circ\text{C}$ . One exception was  $\text{S}_2\text{O}_3^{2-}$  in spent sulphite liquor which appeared to be stable only up to about five days of storage. Following this period, a sharp decrease in concentration was observed regardless of the storage temperature. In most cases prolonged storage for up to 69 days produced little additional changes in concentrations compared to the results obtained after 20 days.

Based on the results of these storage experiments, the following recommendations are given for sample preservation:

#### Recommendations

1. Kraft white and black liquors should be analyzed within 3 weeks of sampling. For longer-term storage, exceeding one month, the samples must be refrigerated or, preferably, frozen to minimize errors caused by oxidation of sulphide to thiosulphate.
2. For white water samples containing low levels of sulphur ions, it is best to freeze or at least refrigerate the samples as quickly as possible after collection. Refrigerated samples

should be analyzed within a week. Frozen samples appear to be stable for at least 2-3 weeks.

3. Spent acid sulphite liquors should also be refrigerated or frozen after sample collection. Under these conditions, both  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  are stable for at least 3 weeks. The results also suggest that  $\text{S}_2\text{O}_3^{2-}$  should be determined within about 5 days after sample collection, regardless of the storage temperature. It must be emphasized, however, that the observed rapid degradation of thiosulphate after an initial stable period may not be applicable to other sulphite liquors, and, therefore, additional data are required to confirm this result.

#### CONCLUSIONS

Factors which could affect the accuracy of IC measurements of sulphur species have been identified. The actual magnitude of errors due, for example, to changes in concentration during sample dilution or storage may vary considerably depending on the type of sample and on the relative proportions of sulphur species. The various precautions described in this work for maintaining sample integrity are intended to minimize the extent of these changes, but may not eliminate them completely. Thus, before undertaking IC measurements on a regular basis, it is recommended to establish the validity of the results on the particular samples under consideration, using the general guidelines for sample treatment and preservation provided in this report.

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