THIOSALT BEHAVIOUR IN AQUEOUS MEDIA

YAOVALUK VONGPORM

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By

Yaovaluk Vongporm

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ABSTRACT

Understanding the behaviour of thiosalts is important in acid mine drainage study as thiosalt oxidation results in pH depression. This research focuses on a study of thiosalt kinetics under acidic, neutral and basic conditions in the temperature range typical of receiving ponds. The thiosalt studies performed in this research included a HSC equilibrium study, a study of freeze-thaw stability, and a thiosalt kinetic reactions study.

The purpose of the HSC equilibrium study was to identify the major factors involved in thiosalt behaviour and to use this data to aid in later experimental design. The study of thiosalt equilibrium composition was performed using HSC Chemistry software and these results were statistically analysed by Design-Expert software. According to the analysis, the formation of thiosulphate depends upon its initial concentration, temperature, and pH. The formation of polythionate is also influenced by temperature, pH, and initial polythionate concentrations. Though these results were not unexpected, it was not anticipated that under equilibrium conditions the behaviour of thiosulphate and polythionate would be relatively independent of each other.

As the freeze-thaw cycle has been shown to influence thiosalt speciation, a stability study was conducted to determine the stability of thiosalt species at different pHs. The thiosalts were found to be reasonably stable using a fast-freeze approach, where at pH 2, 4, and 7, most thiosalt concentrations changed within the range of ±6% after fast freezing in liquid nitrogen, storage in a freezer, and thawing in a water bath at 20°C just prior to analysis.

Kinetic experiments were designed and conducted with the purpose of investigating thiosalt reaction kinetics under acidic, neutral, and basic conditions at variable temperatures. According to the results of this study, thiosulphate decomposed to trithionate, sulphate, and tetrathionate at pH 2. At pH 2 and 9, trithionate decomposed to sulphate, thiosulphate and tetrathionate only at 30°C; while at pH 4 and 7, trithionate decomposed to sulphate, thiosulphate and tetrathionate at temperatures of 15°C or greater. At pH 9, tetrathionate decomposed to thiosulphate, trithionate, and sulphate. In a mixture of thiosalt, thiosulphate and trithionate reacted as in the single species experiments, but tetrathionate was more reactive. Generally, the relative rates of decomposition of thiosulphate, trithionate, and tetrathionate were second or higher order. The decomposition rates increased with increasing initial thiosalt concentration and temperature (except for thiosulphate decomposition at pH 9 and 30°C).

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CHAPTER 1

INTRODUCTION

Thiosalts are the salts of sulphur oxyanions produced from the interaction between sulphur-rich ores and oxygen during mining processes. Important thiosalt species include thiosulphate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$), pentathionate ($S_5O_6^{2-}$), and hexathionate ($S_6O_6^{2-}$). The chemical and biological oxidation of thiosalts in natural waters produces acid which can harm aquatic organisms. This is a significant environmental problem for many mining operations in Canada and worldwide.

1.1 Background

1.1.1 Thiosalt Formation and Degradation

Thiosalts are the intermediate products from the interaction between sulphur-rich ores, such as pyrite and pyrrhotite, and oxygen during certain mining processes. The prefix "thio" is used when a sulphur atom replaces an oxygen atom in the compound(s). Thiosalts are mostly generated in the grinding and flotation processes. Thiosalt species include thiosulphate ($S_2O_3^{2-}$) and polythionate ($S_nO_6^{2-}$, $3 \leq n \leq 6$) (Dinardo and Sally, 1998). Thiosulphate, trithionate ($S_3O_6^{2-}$), and tetrathionate ($S_4O_6^{2-}$) are major thiosalt species produced in the typical mining processes. Their concentrations in mining wastewater are in the range of less than 30 to 1000 ppm. Higher polythionates are usually present at lower concentrations. The concentration of pentathionate, which is the most common higher polythionate, in mining wastewater is approximately 0-60 ppm (Dinardo and Salley, 1998; Wolkoff and Larose, 1975; Gould et. al, 2004).

Factors effecting thiosalt formation during a mining process are mineral sulphide content, flotation period, temperature, flotation stir rate, pH, and ore particle size (Wasserlauf and Dutrizac, 1982).

Thiosalt equilibria in different environments can be described generally by (Lyons and Nickless, 1968):

$$S_nO_6^{2-} + S_2O_3^{2-} \underset{OH^-}{\overset{H^+}{\leftrightarrow}} S_{n+1}O_6^{2-} + SO_3^{2-} \tag{1.1}$$

Accordingly, the overall interchange of trithionate, tetrathionate and pentathionate under neutral conditions can be explained by a disproportionation reaction (Lyons and Nickless, 1968):

$$2S_4O_6^{2-} \rightarrow S_5O_6^{2-} + S_3O_6^{2-} \tag{1.2}$$

1.1.2 Environmental Problem

The chemical and biological oxidation of thiosalts in receiving waters generates acid that can harm aquatic organisms. Additional thiosalt impacts on natural aquatic systems are sediment metal leaching, and reduction of dissolved oxygen and buffering capacity (Dinardo and Salley, 1998).

The chemical oxidation of thiosalts in the environment is dominated by hydrolysis reactions. Wasserlauf and Dutrizac (1982) suggested thiosalt hydrolysis reactions as follows:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \tag{1.3}$$

$$4S_4O_6^{2-} + 5H_2O \rightarrow 7S_2O_3^{2-} + 2SO_4^{2-} + 10H^+ \tag{1.4}$$

Biological oxidation of thiosalts occurs when certain bacteria species in the genus *Thiobacillus* in natural waters oxidize thiosalt from contaminated mining wastewater. Examples of these bacteria include *Thiobacillus thiooxidans*, *Thiobacillus thioparus*, *Thiobacillus neapolitanus*, *Thiobacillus novellus*, and *Thiobacillus denitrificans* (Dinardo and Salley, 1998). The acid produced from thiosalt biological oxidation also lowers the pH of the natural waters. Thiosalt biological oxidation reactions were proposed by Kelly and Tuovinen (1975):

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \tag{1.5}$$

$$S_3O_6^{2-} + 2O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ \tag{1.6}$$

$$2S_4O_6^{2-} + 7O_2 + 6H_2O \rightarrow 8SO_4^{2-} + 12H^+ \tag{1.7}$$

The trend toward decreasing pH varies seasonally. In summer, bacteria effectively oxidize thiosalts in mining wastewater and produce acid causing pH drops in watercourses. When temperatures decrease in fall, bacterial oxidation efficiency is lower, resulting in thiosalt accumulation in the receiving waters with a lower amount of acid produced. In winter, bacteria inefficiently oxidize thiosalts; as a result, thiosalt concentration will be highest with the minimum acid generated. As temperature increases again in spring, bacterial efficiency increases, causing a reduction in thiosalt concentration with an increase in acid production. (Dinardo and Sally, 1998; Fyfe, 2006; Butler, 2006)

1.1.3 Mitigation and Control

At present, the widely used method for managing thiosalt-contaminated wastewater is to allow natural microbial oxidation in effluent holding ponds. To ensure the discharged effluent is not too acidic, lime is introduced to neutralise the acid produced by the microorganisms before discharging the effluent into natural receiving waters. However, thiosalts remaining in the effluent can undergo further oxidation to sulphuric acid after discharge and thus can continue to pose a threat to aquatic organisms. Furthermore, bacterial efficiency is not stable throughout the year in northern climates making it difficult to ensure complete oxidation of the thiosalts prior to discharge. (Dinardo and Salley, 1998; Gould et al, 2004)

A laboratory scale study conducted for Thiosalts Consortium by Gould et al. (2004) investigated factors effecting microbial oxidation of thiosalts in tailing ponds. Their study showed that temperature and oxygen are the limiting factors for microbial thiosalt oxidation.

In work for Thiosalts Consortium - Phase II (Dinardo and Salley, 1998), many methods of treatment for thiosalt-contaminated wastewater have been studied. Methods capable of completely eliminating thiosalts contaminating mining wastewater include ozonation, chlorination, hydrogen peroxide, SO_2-air, chalcopyrite catalysis, reverse osmosis, iron reduction and alkaline pressure oxidation. However, initial investment in infrastructure and operating cost is a very important factor in method selection. The Thiosalts Consortium Management Committee selected three methods for further investigation, which include biological oxidation in rock-packed reactors, biological oxidation in rock-packed reactors with hydrogen peroxide polishing, and hydrogen peroxide only. The results from the investigation indicated that biological oxidation in rock-packed reactors is capable of removing thiosalts almost entirely. In addition, operation at the temperature of 1.0°C is possible and this method is the most cost-effective.

1.2 Purpose of the Research

This research focuses on the kinetics of thiosalt formation and degradation in aqueous media. Experiments were designed and conducted to determine the parameters that directly impact thiosalt kinetics in the conditions that approximated the receiving ponds.

Chapter 2 presents a literature review of previous thiosalt studies conducted under different conditions and a review of the concept of capillary electrophoresis (CE) which was used in the thiosalt analysis.

The HSC equilibrium study, presented in Chapter 3, is a preliminary study performed to identify major species and parameters likely to have an impact on the reactions of each thiosalt species under equilibrium. Parameters being examined include temperature, pH, and concentrations of thiosalts.

CE was used to analyze thiosalt concentrations throughout this research. The CE results studies presented in Chapter 4 were performed with the intention to investigate the reproducibility and variability associated with the CE results.

In order to determine the stability of thiosalt species under freeze and thaw conditions, a stability study was performed for each thiosalt species at pHs of 2, 4, 7, and 9. The freeze-thaw stability study is presented in Chapter 5.

In addition, experiments were conducted to determine thiosalt reaction kinetics at acidic (pH 2 and 4), neutral (pH 7) and basic (pH 9) conditions at temperatures of 4°C, 15°C, and 30°C. The thiosalt species examined were thiosulphate, trithionate, tetrathionate, and a mixture of these three thiosalt species. The thiosalt kinetic study is presented in Chapter 6.

Chapter 7 provides the conclusions of thiosalt studies conducted in this research and recommendations for future work.

1.3 Research Method

For the HSC equilibrium study presented in Chapter 3, HSC Chemistry software (Version 5.1, Outokumpu Technology) was used to calculate equilibrium compositions of thiosalt species under equilibrium. Design-Expert software (Version 6.0.3, Stat-Ease, Inc. 2000) was used to statistically analyse the results from the HSC software to determine significant factors effecting thiosalt formation under equilibrium conditions.

Chapter 4 presented the reproducibility and variability studies of the CE results. The reproducibility of the CE method was determined by comparing the results of replicate analyses of the same sample solutions for each of the thiosalts. CE results of different sample solutions with the same thiosalt concentration were used to determine the variability. The CE results investigated in the variability study were collected from the data for the thiosalt kinetic study presented in Chapter 6.

The freeze-thaw stability study presented in Chapter 5 was performed by comparing the thiosalt concentrations determined by CE from samples analysed immediately to samples frozen then analysed.

The thiosalt kinetic study presented in Chapter 6 was conducted by determining thiosalt and sulphate concentration as a function of time under different pHs and temperatures.

Druschel et al. (2003a) studied tetrathionate rearrangement under acidic conditions at temperature range of 4-70°C. The results showed that at pH 1, tetrathionate undergoes a disproportionation reaction to form trithionate and pentathionate. The ratio of trithionate to tetrathionate to pentathionate is 25: 50: 25. On the other hand, when the pH is in the range of 1-2, tetrathionate rearrangement to trithionate and pentathionate proceeds very slowly.

Xu and Schoonen (1995) studied thiosulphate decomposition in buffered solutions at pHs between 2.9 and 5.2 at 20°C. Their study illustrated that the thiosulphate disproportionation rate is greater than the rate of oxidation by oxygen. Sulphite and elemental sulphur are the major products from thiosulphate disproportionation, while sulphate was found as a minor product. Thiosulphate decomposition reaction was suggested as follows:

$$2S_2O_3^{2-} + H^+ \rightarrow HSO_3^{2-} + SO_3^{2} + 2S \qquad (2.1)$$

Sulphate forms from sulphite oxidation by oxygen. Therefore, sulphate concentration increases with increasing dissolved oxygen concentration. Xu and Schoonen (1995) also noted that the experimental solutions were cloudy as a result of elemental sulphur formation. Moreover, Xu and Schoonen (1995) reviewed thiosulphate decomposition from several studies as summarized in Table 2.1.

Table 2.1 Thiosulphate reaction products (Xu and Schoonen, 1995)

Conditions	**Decomposition Products**
Weak acid	Sulphite and elemental sulphur
Strong acid	Sulphate and sulphidic sulphur
Neutral or alkaline solution in the presence of certain bacteria	
High temperature solution	
Under acidic conditions with sulphidic sulphur	Hexathionate
In the presence of oxidants; for example, ferric ion (Fe^{3+}) and iodine	Tetrathionate

The study by Meyer and Ospina (1982) on trithionate and tetrathionate decomposition in non-buffered solutions at pH of 3.5 and 4 and temperatures from 20°C to 70°C illustrated that trithionate and tetrathionate decompose to sulphate, elemental sulphur, disulphide, and bisulphide. Although disulphide and bisulphide must be less significant as the authors do not consider them in mass balance calculation or in the proposed reactions. Trithionate and tetrathionate disproportionation reactions can be explained by:

$$6S_3O_6^{2-} + 4H_2O \rightarrow S_8 + 10SO_4^{2-} + 8H^+ \qquad (2.2)$$

$$3S_4O_6^{2-} + 2H_2O \rightarrow \frac{7}{8}S_8 + 5SO_4^{2-} + 4H^+ \qquad (2.3)$$

It was also found that trithionate decomposes faster than tetrathionate, and the decomposition rates increase with rising temperature. Trithionate and tetrathionate underwent interchange. In addition, thiosulphate was found to be a major intermediate product. The primary stages of trithionate and tetrathionate disproportionation were suggested as follows:

$$S_3O_6^{2-} + H_2O \rightarrow HSO_4^- + S_2O_3^{2-} + H^+ \qquad (2.4)$$

$$2S_4O_6^{2-} \rightarrow S_3O_6^{2-} + S_5O_6^{2-} \qquad (2.5)$$

$$3S_3O_6^{2-} \rightarrow S_4O_6^{2-} + 2SO_4^{2-} + 2SO_2 + \frac{1}{8}S_8 \qquad (2.6)$$

Mizoguchi et al. (1976) studied the disproportionation of thiosulphate, trithionate, tetrathionate, and sulfite under acidic conditions at a temperatures ranging from 70-150°C. Their results showed that thiosulphate decomposes to elemental sulphur, tetrathionate, and sulphite under acidic conditions at a temperature of 70°C, but barely decomposes at higher pHs and temperatures. Thiosulphate decomposition reactions under acidic conditions were proposed:

$$5S_2O_3^{2-} + 6H^+ \rightarrow 2S + 2S_4O_6^{2-} + 3H_2O \qquad (2.7)$$

$$S_2O_3^{2-} + H^+ \rightarrow S + HSO_3^- \qquad (2.8)$$

$$3S_2O_3^{2-} + 2H^+ \rightarrow 4S + 2SO_4^{2-} + H_2O \qquad (2.9)$$

It was observed that the amount of tetrathionate formed (Equation 2.7) increases with an increase in solution acidity, then decreases after reaching a peak amount; whereas the amount of sulphite (Equation 2.8) formed continually increases with an increase in solution acidity. As temperature increases from 70°C to 130°C, the amount of tetrathionate formed increases, the amount of sulphite decreases, while the amount of sulphate is stable. Tetrathionate decomposes at temperatures higher than 130°C.

Under acidic conditions at the temperature from 70 to 110°C, trithionate disproportionates to thiosulphate and sulphate, and then thiosulphate formed decomposes to elemental sulphur, tetrathionate, and sulphite. Trithionate decomposition in solutions with intermediate pHs can be illustrated by:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (2.10)$$

At temperature higher than 130°C under an acidic condition, tetrathionate decomposes to elemental sulphur and sulphate. The decomposition reaction can be represented by:

$$3S_4O_6^{2-} + 2H_2O \rightarrow 7S + 5SO_4^{2-} + 4H^+ \qquad (2.11)$$

Thiosulphate is found as an intermediate product; the following equation illustrates tetrathionate decomposition forming thiosulphate.

$$4S_4O_6^{2-} + 5H_2O \rightarrow 7S_2O_3^{2-} + 2SO_4^{2-} + 10H^+ \qquad (2.12)$$

However, it was noted that at 150°C, tetrathionate concentration was most stable at pH 2-3.

At 150°C, sulphite decomposes to thiosulphate and sulphate; subsequently, elemental sulphur, sulphate, and tetrathionate are formed. The sulphite decomposition reaction can be explained by:

$$4HSO_3^- \rightarrow S_2O_3^{2-} + 2SO_4^{2-} + 2H^+ + H_2O \qquad (2.13)$$

The overall thiosalt decomposition pathway under acidic conditions is shown in Figure 2.1.

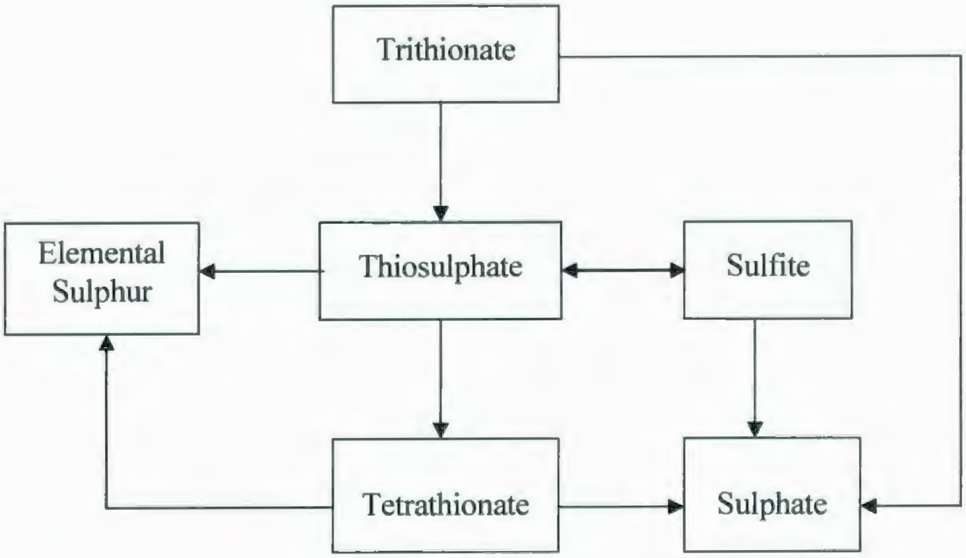

Figure 2.1 Decomposition of thiosulphate, trithionate, tetrathionate and sulfite under acidic conditions (Modified from Mizoguchi et al., 1976)

2.1.2 Basic Conditions

According to Wasserlauf and Dutrizac (1982), under basic conditions, thiosulphate is relatively stable, while polythionates are fairly unstable. Polythionate decomposition products are elemental sulphur, thiosulphate, and sulphite. Polythionate decompostion reactions can be described by (Wasserlauf and Dutrizac,1982):

$$2S_3O_6^{2-} + 6OH \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \tag{2.14}$$

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \tag{2.15}$$

$$2S_5O_6^{2} + 6OH \rightarrow 5S_2O_3^{2-} + 3H_2O \tag{2.16}$$

$$2S_6O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2} + 2S + 3H_2O \tag{2.17}$$

Sulphate forms from sulphite oxidation by oxygen.

$$SO_3^{2-} + \frac{1}{2}O_2 \rightarrow SO_4^{2-} \tag{2.18}$$

Elemental sulphur and sulphite that are produced may react and generate thiosulphate. The order of susceptibility to decomposition from low to high rate is trithionate, tetrathionate, pentathionate, and hexathionate. Their decomposition rates increase with increasing temperature, pH, and presence of nucleophils.

Rolia and Chakrabarti (1982) also investigated the decomposition of thiosulphate, trithionate, and tetrathionate in alkaline solutions. As with Wasserlauf and Dutrizac, their study showed that the products from tetrathionate decompositions at pH > 10 are thiosulphate and trithionate, whereas trithionate decomposition in a pH range of 5.5-12 produces thiosulphate and sulphate (not sulphite as seen in Equation 2.14). Finally, thiosulphate undergoes an oxidation by oxygen to sulphate as illustrated in Figure 2.2. The decomposition rates also increase with increasing temperature and pH. Tetrathionate decomposition reaction in weak base solution was proposed:

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \tag{2.19}$$

Trithionate decomposition reaction was suggested and appears to correspond to trithionate hydrolysis reaction:

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \tag{2.20}$$

Thiosulphate oxidation by oxygen under a basic condition at a temperature range of 75-87°C can be illustrated by:

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \tag{2.21}$$

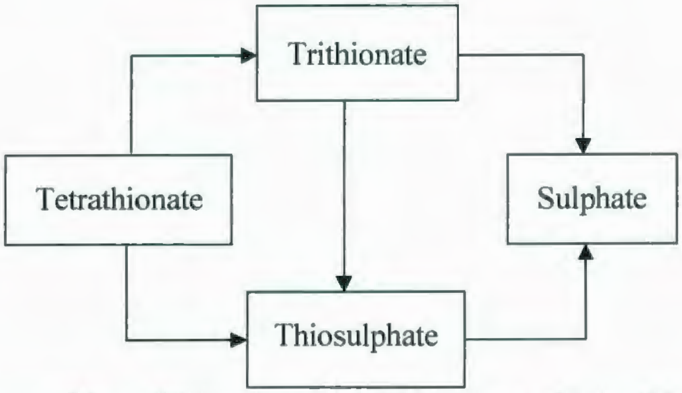

Figure 2.2 Decomposition of thiosulphate, trithionate, and tetrathionate in alkaline solutions (Modified from Rolia and Chakrabarti, 1982)

In summary, under acidic conditions, polythionates are relatively stable; in contrast, thiosulphate is fairly unstable. Thiosalts decomposition products under acidic conditions from various studies reviewed here are summarized in Table 2.2. On the contrary, under basic conditions, thiosulphate is rather stable, whereas polythionates are relatively unstable. Table 2.3 lists polythionates decomposition products under basic conditions from several studies.

Table 2.2 Thiosalt decomposition under acidic conditions from previous studies

Thiosalt species	Conditions	Decomposition products	References
Thiosulphate	pH : 1.95-2.25 Temperature:70-150°C	Elemental sulphur, tetrathionate, sulphite, sulphate	Mizoguchi et al., 1976
	Acidic	Sulphur, sulphate, trithionate, tetratrathioante	Wasserlauf and Dutrizac,1982
	pH : 2.9-5.2 Temperature: 20°C	Elemental sulphur, sulphite	Xu and Schoonen, 1995
Trithionate	Acidic Temperature: 70-110°C	Thiosulphate, sulphate	Mizoguchi et al., 1976
Tetrathionate	Acidic Temperature > 130°C	Elemental sulphur, sulphate	Mizoguchi et al., 1976
	pH 1 Temperature: 4-70°C	Trithionate, pentathionate	Druschel et al., 2003a
Trithionate and tetrathionate	pH : 3.5-4.0 Temperature: 20-70°C	Elemental sulphur, sulphate, disulphide, bisulphide	Meyer and Ospina, 1982

Table 2.3 Thiosalt decomposition under basic conditions from previous studies

Thiosalt species	Conditions	Decomposition products	References
Thiosulphate	Basic Temperature: 75-87°C	Sulphate	Rolia and Chakrabarti, 1982
Trithionate	pH : 5.5-12.0 Temperature: 70-85°C	Thiosulphate, sulphate	Rolia and Chakrabarti, 1982
Tetrathionate	pH $\geq$10 Temperature: 15-85°C	Thiosulphate, trithionate	Rolia and Chakrabarti, 1982
Polythionate	Basic	Elemental sulphur, thiosulphate, sulphite	Wasserlauf and Dutrizac, 1982

2.1.3 Thiosalt oxidation with other chemicals or compounds

Xu and Schoonen (1995) investigated thiosulphate decomposition in the presence of potential catalysts in thiosalt reactions. The results suggested that pyrite, galena, sphalerite, and hematite, except elemental sulphur, can catalyse thiosulphate decomposition to tetrathionate.

Pyrite oxidation forming thiosulphate can be illustrated by the following equation (Luther, 1987).

$$FeS_2 + 6Fe(H_2O)_6^{3+} + 3H_2O \rightarrow Fe^{2+} + S_2O_3^{2-} + 6Fe(H_2O)_6^{2+} + 6H^+ \qquad (2.22)$$

Under acidic conditions with excess ferric ion (Fe^{3+}), typical of an acid mine drainage environment, thiosulphate oxidation via decomposition of a ferric thiosulfate complex results in tetrathionate formation (Williamson and Rimstidt, 1993; Tykodi, 1990).

$$2S_2O_3^{2-} + 2Fe^{3+} \rightarrow 2FeS_2O_3^{+} \rightarrow 2Fe^{2+} + S_4O_6^{2-} \qquad (2.23)$$

However, at pH > 1.7, ferric ion is less available so thiosulphate decomposition by H^+ is faster than thiosulphate decomposition by Fe^{3+} (Williamson and Rimstidt, 1993).

Druschel et al. (2003a) investigated thiosulphate, trithionate, and tetrathionate oxidation at the pH range of 0.4-2.0 in the presence of the ferric ion (Fe^{3+}) and oxygen. The oxidation rates from high to low are thiosulphate, trithionate, and tetrathionate. The major oxidation product of thiosulphate oxidation is tetrathionate, while that of trithionate and tetrathionate is sulphate. Tetrathionate oxidation reaction by Fe^{3+} and oxygen under an acidic condition can be shown as:

$$S_4O_6^{2} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^+ \qquad (2.24)$$

Borda et al. (2003) reported that hydroxyl radical formed on pyrite surfaces from a reaction between water and ferric ion may participate in sulphur oxidation reactions. Accordingly, Druschel et al. (2003b) investigated trithionate and tetrathionate oxidation under acidic conditions (pH 0.5-2.0) by hydroxyl radicals generated utilizing Fenton's reagent. The results illustrated that the rate of trithionate and tetrathionate oxidation with hydroxyl radical under acidic conditions is higher than with ferric ion or oxygen.

Additionally, according to Wasserlauf and Dutrizac (1982), several chemical reagents have been used to oxidize thiosalt to sulphate. These chemical reagents are iodine, potassium permanganate, potassium dichromate, ceric sulphate (Cerium (IV) Sulphate), bromine, hypochlorite, chlorine, and hydrogen peroxide.

Suzuki (1999) suggested the following thiosulphate oxidation reactions by iodine and chlorine:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \qquad (2.25)$$

$$S_2O_3^{2-} + 4Cl_2 + 5H_2O \rightarrow 2SO_4^{2-} + 8Cl^- + 10H^+ \qquad (2.26)$$

2.1.4 Thiosalt stability study

Wasserlauf and Dutrizac (1982) reviewed thiosalt stability under acidic, neutral and basic conditions. Thiosalt species studied were thiosulphate, trithionate, and tetrathionate. The pHs of the solutions were 3, 4, 7, and 10. Thiosalt solutions were prepared and purged with nitrogen. One sample bottle was kept in the dark at room temperature. The other sample bottle was frozen. Thiosalt concentrations were analyzed every week for the period of five weeks. The frozen samples were thawed before the analysis. The results indicated that concentrations of total thiosalt were 7-15% lower than the initial concentrations for the samples that were kept at room temperature; while total thiosalt concentrations were 1-10 % lower than the initial concentrations for the samples that were frozen. It was noted that elemental sulphur was formed in the sample bottle kept at room temperature, concluded from the observation that the sample became cloudy during the experiment.

Druschel et al. (2003a) conducted a thiosalt stability experiments for trithionate and tetrathionate oxidation by the ferric ion (Fe^{3+}) at pH of 0.4-2.0. The results demonstrated that concentrations of sulphur species during tetrathionate oxidation experiments do not significantly change after storage in a 4°C refrigerator for several days. However, the trithionate oxidation reaction is very fast at low temperature (4°C).

2.2 Capillary Electrophoresis (CE)

Capillary electrophoresis is a separation technique that can be used for the separation of ionic species based on their mobility in an electrolyte solution under the influence of an electric field. A factor affecting the mobility of charged species is their charge to size (hydrodynamic volume) ratio; a small ion with high charge will migrate faster than a large ion with low charge (Weinberger, 2000; Dean, 1995). This type of separation based on ion mobility is often called capillary zone electrophoresis (CZE).

A bare fused silica capillary is treated with sodium hydroxide (~1.0 M) to activate the silanol groups, which leads to electrokinetic or electroosmotic flow (EOF) in the capillary when a potential is applied. The capillary is then equilibrated with background electrolyte (BGE) before sample injection. The BGE is usually composed of a buffer solution with a fixed pH. The pH influences the speed of EOF, fastest at pH > 9.0, nearly non-existent at pH < 4.0, and whether specific analytes are ionized. For example weak acids are only fully ionized at pHs sufficiently above their pK_a. A high voltage power supply is used to apply potential to the inlet and outlet vials (Figure 2.3). In positive mode EOF is toward the cathode (detector end), anions travel toward the anode, while cations travel toward the cathode. In negative mode, the EOF is away from the detector because the anode and cathode positions are switched; thus the anions migrate toward the detector because the anode is now at the outlet/detector end of the capillary. Separation occurs due to the difference in the mobility of each charged species in the background electrolyte. A detector near the capillary outlet detects each charged species as it reaches the detector window; differentiation between species requires migration times to be different. Each detected species is represented by a peak in an electropherogram (Weinberger, 2000; Dean, 1995). The concentrations of thiosalt were subsequently calculated by comparing the peak area produced using a standard solution.

CE methods can be tailored to provide very high resolution separations. Compared to HPLC (high performance liquid chromatography), capillary electrophoresis is superior in terms of speed, efficiency, selectivity, relative ease of method development, flexibility, and reagent consumption. On the other hand, the disadvantages of capillary electrophoresis compared to HPLC are detection sensitivity because of low volumes (mass loading), precision, and durability of the capillary (Weinberger, 2000).

Figure 2.3 shows a basic diagram of capillary electrophoresis. The main components of a CE system are (Weinberger, 2000; Dean, 1995; Millner, 1999):

- Capillary

  The capillary is normally made of fused silica with a polyimide coating. The advantage of fused silica is its UV transparency and ability to transfer heat. The polyimide coating enhances the stability and flexibility of the capillary. Typical capillaries have inner diameter of 25 to 100 µm.

- Background electrolyte (BGE)

Background electrolyte can be very complex or simple; the composition can influence ionization, EOF, migration behaviour, sensitivity, and peak shape. In CZE the BGE is often a simple buffer solution which is designed to maintain consistent EOF and ionization of the analytes. To minimize joule heating, the conductivity (current) must be kept low, thus the typical buffer solution concentration range is 10-100 mM.

- High voltage power supply

To induce migration of analytes and EOF, a high voltage power supply is used to apply potential across the capillary at electrodes placed in the inlet and outlet vials containing BGE. The maximum voltage supply for conventional CE is approximately 30 kV.

- Detector

Commercially available detection systems use fluorescence, UV-vis absorption, conductivity detection and mass spectrometry. Among these techniques, ultraviolet-visible absorption is currently the most widely used.

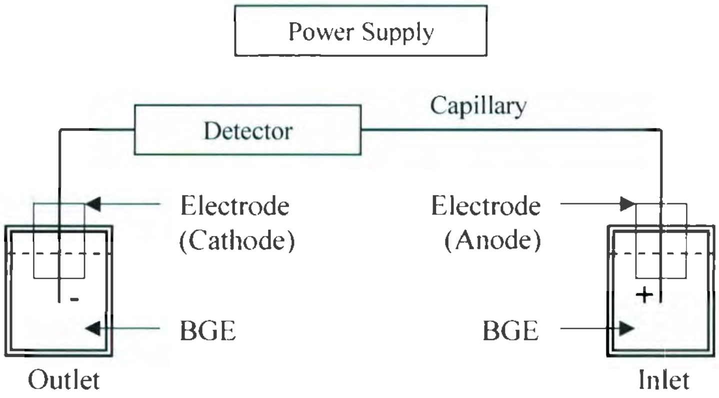

Figure 2.3 CE system diagram for positive mode (Adapted from Weinberger, 2000)

CHAPTER 3

HSC EQUILIBRIUM STUDY

A preliminary study was designed and performed to identify major species and parameters likely to have an impact on the reactions of each thiosalt species under equilibrium conditions. Parameters examined included temperature, pH, and concentrations of thiosalt.

3.1 Materials and Methods

The equilibrium compositions of thiosalt species under different conditions were computed by HSC Chemistry (Version 5.1, Outokumpu Technology, Finland). The results from the HSC software were then statistically analysed by Design-Expert (Version 6.0.3, Stat-Ease, Inc. 2000, USA) to determine significant factors affecting thiosalt formation under equilibrium conditions.

3.1.1 Software

3.1.1.1 HSC Chemistry

HSC Chemistry is designed to calculate probable chemical reactions and equilibrium compositions using thermodynamic properties of chemical elements or compounds. Major properties of chemical compounds used in these calculations are enthalpy (H), entropy (S), and heat capacity (C_p); accordingly, the name of the software is derived from these thermodynamic parameters. The software provides several calculation functions; for example, chemical reaction equations, heat and material balances, heat loss calculations, and equilibrium compositions. Additionally, it contains a thermochemical database of more than 17,000 chemical compounds. Typical characteristics of chemical compounds in the HSC Chemistry database are molecular weight, enthalpy, entropy, heat capacity, density, colour, and water solubility (HSC Chemistry, 2000).

HSC Chemistry computes chemical equilibria using thermodynamic properties of elements or compounds. The Gibbs energy minimization was used to calculate the equilibrium compositions. A system reaches the most stable phase when the Gibbs energy reaches its minimum point at a fixed mass balance, constant pressure, and temperature. Consequently, at this point, the equilibrium compositions can be calculated (HSC Chemistry, 2000). However, it should be noted that the software does not consider reaction kinetics. Therefore, the equilibrium analysis is simply a tool to aid in later experimental design as the results from this analysis will suggest potential factors affecting thiosalt kinetics reactions.

The following equations are used to calculate thermodynamic properties of elements or compounds in the HSC Chemistry (HSC Chemistry, 2000).

- Enthalpy (H) calculation

$$H(T) = H_f(298.15) + \int_{298.15}^{T} C_p dT + \sum H_{tr} \tag{3.1}$$

H_f = Enthalpy of formation at 298.15 K

H_{tr} = Enthalpy of phase transformation

C_p = Heat capacity

T = Temperature

- Entropy (S) calculation

$$S = S(298.15) + \int_{298.15}^{T} (\frac{C_p}{T})dT + \sum \frac{H_{tr}}{T_{tr}} \tag{3.2}$$

S (298.15) = The standard entropy at 298.15 K.

- Heat capacity (C_p) calculation

$$C_p = A + 10^{-3}BT + 10^5 CT^{-2} + 10^{-6}DT^2 \tag{3.3}$$

A, B, C, and D are heat capacity coefficients

- Gibbs energy (G) calculation

$$G = H - TS \tag{3.4}$$

3.1.1.2 Design-Expert

Design-Expert performs statistical analysis for design of experiments. It is a registered trademark of Stat-Ease, Inc. The software provides many statistical functions including (Design-Expert, 2000):

- Two-level factorial: Used to investigate important factors with numerical values affecting a process or system.

- General factorial: Used to examine important categorical factors affecting a process or system.

- Response surface method: Used to identify proper conditions/factors to obtain an optimal process or product.

3.1.2 Experimental Method

In order to identify important factors effecting thiosalt formation, an equilibrium study was performed on HSC Chemistry. Factors examined included temperature, pH, and concentrations of thiosulphate, trithionate, tetrathionate, and pentathionate. Table 3.1 lists the ranges of these factors used in this work. The ranges were based on those typically encountered in the receiving pond at a mine.

HSC Chemistry calculated equilibrium compositions of each thiosalt species and other possible chemical species in a system with primary elements of sulphur, oxygen and hydrogen. The thiosalt species under investigation are thiosulphate, trithionate, tetrathionate, and pentathionate. Based on the Eh-pH diagram of intermediate sulphur species constructed by Druschel et al. (2003a) with suppressing sulphate, the other possible species which contain sulphur, oxygen and hydrogen are SO_3^{2-}, S_8, $S_2O_6^{2-}$, HS^-, H_2S, H_2SO_3, HSO_3^-, and HSO_5^-. However, sulphate was included in the equilibrium calculation of the current study.

The results from HSC Chemistry were statistically analysed by Design-Expert using two-level factorial with one center point method to identify significant factors likely to have impacts on the formation of each thiosalt species.

Table 3.1 Factors and ranges for HSC equilibrium study

Factors	Minimum	Maximum
Thiosulphate Concentration	100 ppm	500 ppm
Trithionate Concentration	100 ppm	500 ppm
Tetrathionate Concentration	100 ppm	500 ppm
Pentathionate Concentration	100 ppm	500 ppm
pH	1	8
Temperature	-5°C	40°C

3.2 Results and Discussion

Equilibrium amounts of thiosalt species and other possible sulphur species under different conditions calculated from HSC Chemistry are shown in Appendix A. Table 3.2 shows an example of these results. Appendix B shows the statistical results from Design-Expert analysis. Table 3.3 summarized the overall results.

Table 3.2 Example of the results from HSC equilibrium calculation

Initial Thiosalt Concentration (ppm)				pH	Temp	Thiosalt species formed (ppm)			
$S_2O_3^{2-}$	$S_3O_6^{2-}$	$S_4O_6^{2-}$	$S_5O_6^{2-}$		°C	$S_2O_3^{2-}$	$S_3O_6^{2-}$	$S_4O_6^{2-}$	$S_5O_6^{2-}$
100	100	100	100	1	-5	2E-03	2E-21	9E-05	2E-19
500	100	100	100	1	-5	4E-03	5E-21	3E-04	6E-19
100	500	100	100	1	-5	4E-03	7E-21	4E-04	7E-19
100	100	500	100	1	-5	4E-03	6E-21	4E-04	7E19
100	100	100	500	1	-5	4E-03	5E-21	3E-04	6E-19
500	500	500	500	1	-5	9E-03	3E-20	2E-03	5E-18
100	100	100	100	8	40	4E-01	6E-20	3E-05	6E-19
500	100	100	100	8	40	2	2E-20	1E-05	3E-19
100	500	100	100	8	40	4E-01	7E-19	4E-04	9E-18
100	100	500	100	8	40	4E-01	5E-19	4E-04	7E-18
100	100	100	500	8	40	4E-01	5E-19	3E-04	6E-18
500	500	500	500	8	40	7E-01	4E-18	4E-03	9E-17

Table 3.3 Statistically significant factors and their contributions to the formations of thiosulphate, trithionate, tetrathionate and pentathionate from the equilibrium study

Significant Factors	Species Formed			
	Thiosulphate	**Trithionate**	**Tetrathionate**	**Pentathionate**
1	pH, 46.7%	Temperature, 73.4%	pH, 44.5%	Temperature, 60.6%
2	Temperature, 45.5%	pH, 20.1%	Temperature, 40.1%	pH, 28.9%
3	Initial thiosulphate concentration, 2.6%	Initial trithionate concentration, 1.8%	Initial trithionate concentrathion, 4.3%	Initial trithionate concentrathion, 2.9%
4		Initial tetrathionate concentration, 1.4%	Initial tetrathionate concentration, 3.4%	Initial tetrathionate concentration, 2.4%
5		Initial pentathionate concentration, 1.2%	Initial pentathionate concentration, 3.0%	Initial pentathionate concentration,, 2.2%

3.2.1 Thiosulphate

According to Table 3.3, the significant factors effecting thiosulphate formation from thiosalt species are pH, temperature, and initial thiosulphate concentration. Among these significant factors, pH and temperature are more significant effects than initial thiosulphate concentration. The maximum contribution to thiosulphate formation is pH; temperature provides the second-highest contribution, while initial thiosulphate concentration has the minimum contribution. Although, from Table 3.2, it seems that initial polythionate concentrations may effect thiosulphate formation; the statistical analysis has shown no significant effect of initial polythionate concentrations on thiosulphate formation. All of the three significant factors are positively correlated with thiosulphate formation, as thiosulphate formation is high at high pH, temperature, and initial thiosulphate concentration. Figure 3.1 illustrates graphically the important factors affecting thiosulphate formation. Mizoguchi et al. (1976), Wasserlauf and Dutrizac (1982), and Xu and Schoonen

(1995) proposed the instability of thiosulphate under acidic conditions. Correspondingly, the results from HSC equilibrium study are consistent with these previous studies as the amount of thiosulphate formed in low pH solutions is lower than in higher pH solutions.

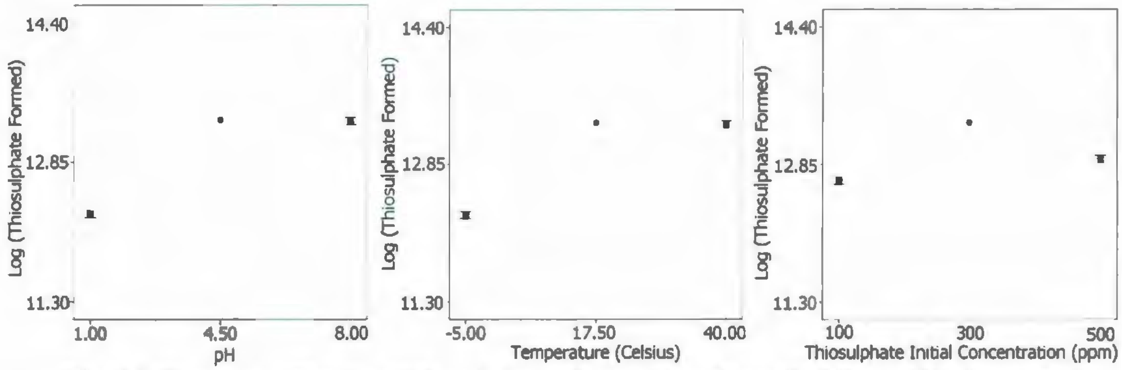

Fig 3.1 Factors affecting thiosulphate formation from HSC equilibrium study

3.2.2 Polythionate

According to Table 3.3, the significant factors effecting polythionate (trithionate, tetrathionate and pentathionate) formation are temperature, pH and initial concentrations of polythionate. It can be seen from Table 3.3 that temperature and pH impart considerably greater effects than initial polythionate concentration. Temperature has a higher effect on trithionate and pentathionate formation than pH. On the other hand, for tetrathionate formation, pH provides a slightly larger effect than temperature.

Among initial polythionate concentrations, initial trithionate concentration has the maximum effect on polythionate formation; tetrathionate gives the second-highest contribution, whereas pentathionate has the least effect. Though, from Table 3.2, it seems that initial thiosulphate concentrations may effect polythionate formation; the statistical analysis has shown that initial thiosulphate concentration provides no effect on polythionate formation.

Temperature and initial polythionate concentrations generate positive effects on polythionate formation as polythionate formations are high at higher temperatures and high initial concentrations of polythionate. However, pH creates a negative effect on polythionate formations as the amount of polythionate formed is low at high pH. Figure 3.2- 3.4 illustrates graphically the important factors affecting polythionate formation.

Wasserlauf and Dutrizac (1982), and Rolia and Chakrabarti (1982) suggested the instability of polythionate under basic conditions. Correspondingly, the results from HSC equilibrium study are compatible with these previous studies.

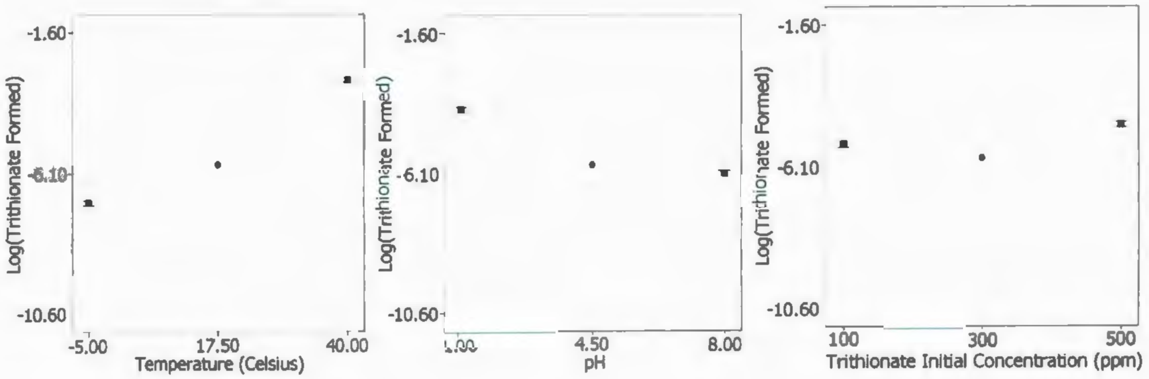

Fig 3.2 Factors affecting trithionate formation from HSC equilibrium study

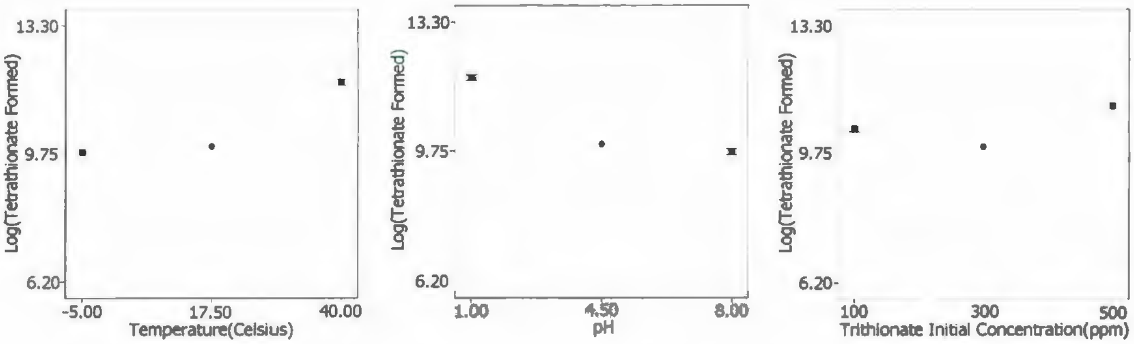

Figure 3.3 Factors affecting tetrathionate formation from HSC equilibrium study

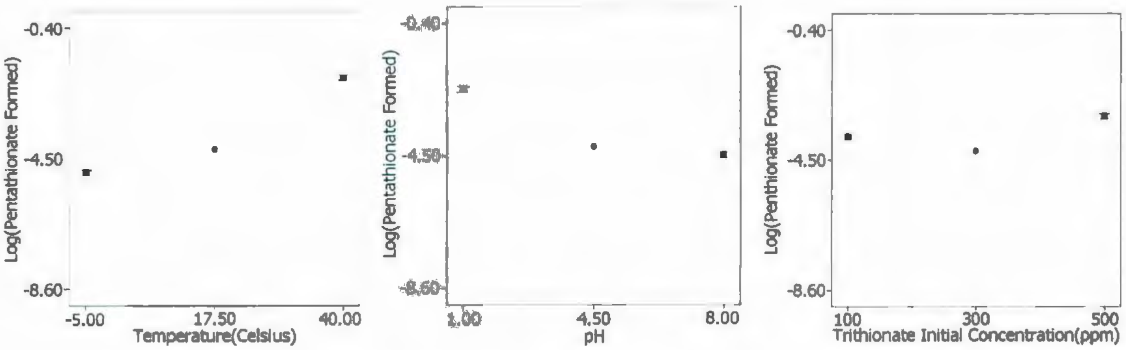

Figure 3.4 Factors affecting pentathionate formation from HSC equilibrium study

3.3 Summary

The thiosalt equilibrium study was designed and conducted to identify major species and parameters likely to have an impact on the reactions of each thiosalt species. From the HSC equilibrium study, temperature and pH have strong influences on thiosalt formation. In general, initial thiosulphate concentration has an impact on only thiosulphate formation, whereas initial polythionate concentration affects only polythionate formation. Therefore, thiosulphate and polythionate formations are relatively independent of each other under equilibrium conditions. However, the literature presented in Chapters 1 and 2 illustrated that thiosulphate and polythionate are usually related in kinetics as illustrated by (Lyons and Nickless, 1968):

$$S_nO_6^{2-} + S_2O_3^{2-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} S_{n+1}O_6^{2-} + SO_3^{2-} \tag{3.1}$$

Temperature and initial thiosalt concentrations produce positive effects on thiosalt formation as thiosalt formation is high at high temperature, and high initial thiosalt concentration. On the other hand, pH creates a positive effect on thiosulphate formation but a negative effect on polythionate formation. Accordingly, at high pH, thiosulphate formation is high, but polythionate formation is low.

The results from HSC Chemistry equilibrium study are compatible with the studies of Mizoguchi et al. (1976), Wasserlauf and Dutrizac (1982), Xu and Schoonen (1995) and Rolia and Chakrabarti (1982) which proposed the instability of thiosulphate under acidic conditions and the instability of polythionate under basic conditions.

Since the HSC Chemistry equilibrium calculation does not consider reaction kinetics; the equilibrium analysis is simply a tool to aid in later experimental design. Although these results may not translate directly to the experimental study of kinetics due to the reaction rates which could be slow as equilibrium is approached, they remain a useful tool for design of experiments. Later thiosalt reaction kinetic study would focus on temperature and pH as the results of this study suggested that these factors have strong effects on thiosalt formation.

CHAPTER 4

CE RESULTS, REPRODUCIBILITY, AND VARIABILITY

Thiosalt can be determined by various methods including titrimetric method, ion exchange, and capillary electrophoresis (CE). Titrimetric method determines bulk thiosalt, while ion exchange metod can be used for thiosalt species separation but it is relatively time-consuming and is not as sensitive. CE was used to analyze thiosalt concentrations in this research due to its advantages in speed, efficiency, and sensitivity. CE was used in the freeze-thaw stability study presented in Chapter 5 and in the thiosalt kinetic study presented in Chapter 6. This chapter provides analyses of the results obtained from CE including a reproducibility study and a determination of the variability of CE results.

4.1 Reproducibility of CE results

Reproducibility was examined by comparing the peak area (Absorbance (mAU) × time (s)) of thiosalt analyzed by CE from two analyses of the same thiosalt sample solution.

4.1.1 Materials and Method

4.1.1.1 Thiosalt Compounds

Thiosalt compounds utilised in this study were thiosulphate, trithionate, and tetrathionate. Thiosulphate and tetrathionate are commercially available. Trithionate is not commercially available and was synthesized by a method modified from Kelly and Wood

(1994). Pentathionate was not investigated in this research because it is usually found in trace concentrations and is difficult to synthesize.

Sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) was obtained from Merck. The molecular weight is 248.18 g. The purity is 99.5-101.0%. Potassium tetrathionate ($K_2S_4O_6$) was obtained from Sigma-Aldrich. The molecular weight is 302.46 g. The purity is more than 98.0%.

Sodium trithionate ($Na_2S_3O_6$) was synthesized by a method adapted from Kelly and Wood (1994) as follows:

- Dissolve 15 g of $Na_2S_2O_3 \cdot 5H_2O$ in 9 mL of water. Cool the solution to 1°C with continuous stirring.
- Slowly add 14 mL of 30% hydrogen peroxide to the solution.
- Stop stirring. Keep the solution in ice for 1-2 hours. Sodium sulphate will crystallise.
- Remove the crystallised sodium sulphate by suction filtration. Wash with 10 mL ethanol.
- Transfer the solution to a beaker, cool to 3°C. Add 25 mL of ice-cold ethanol. Leave the solution at 0-3°C for 1 hour. Sulphate will crystallise.
- Remove the crystallised sulphate by suction filtration. Wash with 20 mL of ice-cold ethanol.
- Transfer the solution to a beaker with 100 mL cold ethanol. Stir and leave the solution at 3°C for 1-2 hours.

- Sodium trithionate ($Na_2S_3O_6$) will crystallize. Remove the crystallized sodium trithionate by suction filtration, wash with 5 mL ethanol, 5 mL of acetone, and leave in a desiccator.

This method provides 6 g of Sodium trithionate with 96-100 % purity. The molecular weight is 238.17 g. Thiosalt sample solutions were prepared in nanopure water (purified by NANOpure Diamond Analytical and UV Systems Deionization, Barnstead International).

4.1.1.2 Thiosalt Analysis

O'Reilly et al. (2003) developed a method for the separation of thiosulphate, trithionate, tetrathionate, pentathionate, and the gold (I) thiosulphate complex (Au $(S_2O_3)_2^{3-}$) by capillary electrophoresis with UV detection. The method used to analyze thiosalt concentrations in this research was modified from O'Reilly et al. (2003) as follows.

- CE: Agilent 1602 capillary electrophoresis equipped with an onboard UV-visible diode-array detector
- Capillary: Simplus brand, MicroSolv Technology Corporation made of bare fused silica (untreated), 50 μm inner diameter, 48.5 cm total length, and 40 cm effective length
- Background electrolyte: 50 mM BIS-TRIS adjusted to pH 6 with concentrated sulphuric acid and filtered with a 0.2 μm nylon filter before use
- CE vial: 1 mL polypropylene vial with polyurethane snap cap, Agilent Technologies
- Capillary flushing solution
    - 1 N Sodium Hydroxide (NaOH) for 15 minutes

  - BGE for 10 minutes

- Injection: Pressure 50 mbar for 10 seconds
- Voltage: 30 kV
- Voltage supply polarity: Negative
- Temperature: 23°C
- Detection wavelength/Slitwidth:
  - Thiosulphate and tetrathionate : Signal 214/10 nm
  - Trithionate: Signal 195/4 nm
  - Reference:
  - Thiosulphate and tetrathionate : 320/5 nm
  - Trithionate: Off

4.1.2 Experimental Method

The CE reproducibility study was conducted by preparing 500 ppm thiosalt solutions in nanopure water. The solutions were filtered using a syringe with 0.2 μm nylon filter and transferred to a CE vial. Analysis of thiosalt concentrations was performed twice. The difference in thiosalt peak area (mAU*s) obtained from the first and second analysis was subsequently calculated.

4.1.3 Results and Discussion

Peak areas of thiosulphate, trithionate, and tetrathionate from the first and second CE analysis were compared. The differences in peak areas of each thiosalt species were calculated. Table 4.1 shows the results of this study. In general, the average percent difference in peak areas between the first and the second analysis is in the range of 2-4% for all thiosalt species studied. Thiosulphate has the minimum average percent difference (2.9), while trithionate has the maximum percent difference (3.5). Therefore thiosulphate has the maximum CE analysis reproducibility, while trithionate has the minimum CE analysis reproducibility.

Table 4.1 Peak area (mAU*s) of 500 ppm thiosalt solutions and percent difference

Analysis	Thiosulphate		Trithionate		Tetrathionate	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
1	182	195	170	164	301	275
2	190	197	180	166	309	285
% Difference	4.6	1.2	5.4	1.5	2.7	3.6
Average % Difference	**2.9**		**3.5**		**3.2**	

4.2 Variability of CE Results

This study was conducted with the intention to investigate the dispersion of the results obtained from CE analysis. Mean, standard deviation, and coefficient of variation of the peak area of thiosulphate, trithionate, and tetrathionate from CE analysis were calculated and examined. Variability of CE results was examined by comparing the CE peak area (mAU*s) of different sample solutions with the same thiosalt concentration.

The mean ($\bar{x}$) measures the middle value of a data set and can be calculated by (Iversen and Gergen, 1997):

$$\bar{x} = \frac{x_1 + x_2 + \ldots + x_n}{n} = \frac{\sum x}{n} \qquad (4.1)$$

Where:

x_i = Observations

n = Number of observations

The standard deviation (s) evaluates the distribution of the data around the mean. The more broadly spread out of the data, the larger the standard deviation. The standard deviation of a data set can be calculated by (Iversen and Gergen, 1997):

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}} \tag{4.2}$$

The coefficient of variation (CV) determines the extent of relative variability of a data set and demonstrates the standard deviation as a percent of the mean and can be calculated by (Sanders, 1990):

$$CV = \frac{s}{\bar{x}}(100) \tag{4.3}$$

4.2.1 Experimental Method

Peak areas (mAU*s) of different sample solutions with 500 ppm thiosalt concentration obtained by CE analysis in the thiosalt kinetic study presented in Chapter 6 were collected and are presented in Table 4.2. Analyses were done on different days, with solutions and capillaries replaced as needed. Means, standard deviations, and coefficients of variation of these data were calculated using equations 4.1, 4.2, and 4.3.

Table 4.2 Peak areas (mAU*s) of 500 ppm thiosalt solutions from CE analysis

Thiosulphate	Trithionate	Tetrathionate
162	160	244
163	173	260
186	175	264
185	186	264
167	174	261
175	165	261
168	170	268
176	153	264
175	168	271
187	166	291
187	186	241
179	164	281
195	158	277
174	167	283
169	172	268
190	160	268
203	180	314
197	187	304
194	191	292
197	181	303
195	207	230
196	222	353
206	174	344
180	185	377
175	165	274
183	164	275
186	169	283
176	172	286
169	169	301
182	166	258
191	168	298
192	167	295
205	196	344
197	202	295
194	174	291
195	167	293
196	169	293
196	169	291
196	169	273
178	164	273
185	159	304
184	178	297
201	174	298
202	175	284
193	167	304
196	170	312
203	175	292
202	175	279
200	168	296
179	170	306

4.2.2 Results and Discussion

Table 4.3 illustrates the means, standard deviations and coefficients of variation of the peak area obtained from the CE analysis of 500 ppm thiosalt solutions calculated from the data presented in Table 4.2.

From Table 4.3, the means and standard deviations of the peak areas of thiosulphate and trithionate are fairly similar, while tetrathionate has a much higher mean and standard deviation. Since all these analyses were of 500 ppm solutions, higher means are indicative of higher absorbance at the wavelength of interest and, thus, greater inherent sensitivity for the species. In general the coefficient of variation is a better way to compare the precision of the data since it is a relative value and it can be seen that the value for thiosulphate, trithionate, and tetrathionate are in the range of 6-10%. Peak areas of thiosulphate have the minimum coeffifient of variation, whereas peak areas of tetrathionate have the maximum value. Therefore, peak areas of thiosulphate are the most uniform and peak areas of tetrathionate are the most variable. While better precisions have been reported using CE, these values are reasonable and are satisfactory for the purposes of this work.

Table 4.3 Means, standard deviations and coefficient of variation of CE peak areas for each thiosalt species

Statistic	Thiosulphate	Trithionate	Tetrathionate
Mean (mAU*s)	187	174	288
Standard Deviation (mAU*s)	11.9	12.8	27.4
Coefficient of Variation (%)	6.4	7.4	9.5

4.3 Summary

The reproducibility study was performed by examining the differences in peak areas of thiosalts from two CE analyses of the same thiosalt sample solution. Generally, the average percent difference in peak areas between the first and the second analysis is in the range of 2-4% for thiosulphate, trithionate, and tetrathionate. Thiosulphate provides the maximum CE analysis reproducibility, while trithionate shows the minimum value.

The variability of CE results study was conducted to examine the distribution of thiosalt peak areas obtained from CE analysis of different samples with the same thiosalt concentration. Means, standard deviations, and coefficients of variation of the peak areas of thiosulphate, trithionate, and tetrathionate from CE analysis were calculated and investigated. The coefficients of variation of thiosulphate, trithionate, and tetrathionate are within the range of 6-10%. Peak areas of thiosulphate have the minimum variability, while peak areas of tetrathionate have the maximum variation. Compared to the reproducibility study more factors contribute to the standard deviation, which considered to be a measure of the errors, including changes in capillaries, BGE solutions, and fluctuations in lamp output. These factors can account for the slight differences in trends regarding reproducibility for these two studies.

CHAPTER 5

FREEZE-THAW STABILITY STUDY

The freeze thaw cycle in natural systems and in laboratory conditions has shown that the process can change speciation, thus a stability study was performed for each thiosalt species in order to determine the stability of thiosalt species under freeze and thaw conditions in acidic (pH 2 and 4), neutral (pH 7), and basic (pH 9) solutions. In addition, the results from this study may be used to facilitate thiosalt analysis in further thiosalt studies by providing a means to store samples for longer periods of time without impacting the speciation. The thiosalt species investigated were thiosulphate, trithionate, and tetrathionate. Pentathionate and hexathionate were not investigated in this study because they are usually present at lower concentrations, they are not commercially available, and they are difficult to synthesize.

5.1 Materials and Method

The freeze-thaw stability study involved the comparison of thiosalt concentrations between samples analysed immediately and those frozen then thawed and analysed. Materials required for this study were the thiosalt compounds, pH 4, 7, and 9 buffered solutions, and a solution acidified to pH 2.

5.1.1 Thiosalt Compounds

The thiosalt compounds utilized in the freeze-thaw stability study were thiosulphate, trithionate, and tetrathionate. The details and synthesis method of these thiosalt species have been described in Chapter 4.

5.1.2 Buffered and Non-Buffered Solutions

The freeze-thaw stability study was designed to determine thiosalt stability under acidic, neutral, and basic conditions. The pH values of the solutions used in these experiments were 2, 4, 7, and 9. Xu and Schoonen (1995) investigated thiosulphate reaction kinetic with and without pyrite. The solutions used in their study were 0.1 M acetic acid (pH 2.9), 0.1 M boric acid (pH 5.2), 0.1 M acetic acid-sodium acetate (pH 6.6), and 0.1 M sodium bicarbonate (pH 8.6). The solutions used in the current study were modified from Xu and Schoonen (1995). Buffer solutions were used for experiments at pH 4, 7, and 9. For experiments at pH 2, an acidic, non-buffered solution was employed. All solutions were prepared with nanopure water (purified by NANOpure Diamond Analytical and UV Systems Deionization, Barnstead International). Chemical compounds used in preparing experimental solutions were as follows:

- pH 2: acetic acid

  Glacial acetic acid was diluted with water until pH 2 was reached, measured using a calibrated pH meter.

- pH 4: 50 mM ammonium acetate/ acetic acid

Dissolve 0.3854 g of ammonium acetate in 70 mL of nanopure water. Add 3 mol/L glacial acetic acid until pH is 4. Add nanopure water to get 100 mL solution.

- pH 7: 50 mM ammonium dihydrogenphosphate /ammonium hydrogenphosphate

  Dissolve 0.2416 g of ammonium dihydrogenphosphate and 0.3803 g of ammonium hydrogenphosphate in 70 mL of nanopure water. Check the pH with pH meter and adjust to pH 7 using acetic acid or ammonium hydroxide. Add nanopure water to make 100 mL solution.

- pH 9: 50 mM ammonium acetate /ammonium hydroxide

  Dissolve 0.3854 g of ammonium acetate in 70 mL of nanopure water. Add 3 mol/L ammonium hydroxide until pH is 9. Add nanopure water to get 100 mL solution.

It should be noted that the acids and salts used were chosen so that they did not participate in any pertinent thiosalt equilibria and sodium salts were avoided as they contribute to ion current and joule heating in CE more than bulkier salts (e.g. ammonium). Table 5.1 presents the details of chemical compounds used in this study.

Table 5.1 Details on chemical compounds used in preparing buffered and non-buffered solutions

Chemical compounds	Molecular formula	Molecular weight	Purity	Source
Glacial acetic acid	CH_3COOH	60.05 g	99.7%	Fisher Scientific
Ammonium acetate	CH_3COONH_4	77.08 g	99.99%.	Sigma Aldrich
Ammonium dihydrogenphosphate	$(NH_4)\ H_2PO_4$	115.03 g	99.99%	Sigma Aldrich
Ammonium hydrogenphosphate	$(NH_4)_2HPO_4$	132.06 g	99.99%	Sigma Aldrich
Ammonium hydroxide (aqueous)	NH_4OH	35.04 g	14.8 mol/L	Sigma Aldrich

5.1.3 Thiosalt Analysis

The method used to analyze thiosalt concentrations was modified from O'Reilly et al. (2003) as described in Chapter 4.

5.1.4 Experimental Method

The stability study was conducted by dissolving 0.025 g of each thiosalt compound in 50 mL of buffer (pH 4, 7, and 9) or non-buffered (pH 2) solution in a volumetric flask. The solution was filtered using a syringe (Micro-Mate interchangeable hypodermic syringe, Popper&Sons, inc.) with 0.2 μm nylon filter (17 mm diameter, National Scientific) and transferred to three CE vials. The first vial was immediately analysed for thiosalt concentrations by capillary electrophoresis. The second vial was frozen and stored at -80°C in an ultra low temperature freezer. The third vial was frozen rapidly in liquid nitrogen before storage at -80°C. After keeping the two vials in the freezer for several days (3-5 days), they were removed and thawed in a water bath at a temperature of 20°C (Innova 4230 refrigerated incubator shaker, New Brunswick Scientific) and analyses of thiosalts performed. The experiments were performed twice. Percent differences are calculated using:

$$\%\,\text{Difference} = \frac{\text{Fast/Normal Freeze Conc. - Immediately Analysed Conc.}}{\text{Immediately Analysed Conc.}} \text{x}100 \qquad (5.1)$$

5.2 Results and discussion

Concentrations of thiosulphate, trithionate, and tetrathionate from the freezing samples without liquid nitrogen (normal freeze) and with liquid nitrogen (fast freeze) were compared with the result of concentrations obtained from the immediate analysis. Tables 5.2, 5.3 and 5.4 summarize the calculated percent differences for each thiosalt species at different pH from two trials.

Table 5.2 Percent difference of thiosulphate concentrations between the immediate analysis and the freezing samples without liquid nitrogen (normal freeze) and with liquid nitrogen (fast freeze) at different pHs

pH	First Trial		Second Trial		Average	
	Normal Freeze	Fast Freeze	Normal Freeze	Fast Freeze	Normal Freeze	Fast Freeze
2	-5.80	-3.92	-3.60	2.19	-4.70	-0.86
4	-3.47	-2.69	26.18	1.53	11.36	-0.58
7	10.05	-8.02	27.18	6.49	18.62	-0.76
9	34.24	21.34	29.63	0.86	31.93	11.11

Table 5.3 Percent difference of trithionate concentrations between the immediate analysis and the freezing samples without liquid nitrogen (normal freeze) and with liquid nitrogen (fast freeze) at different pHs

pH	First Trial		Second Trial		Average	
	Normal Freeze	Fast Freeze	Normal Freeze	Fast Freeze	Normal Freeze	Fast Freeze
2	-6.81	-2.20	-23.23	0.90	-15.02	-0.65
4	20.98	-1.42	1.74	2.40	11.36	0.49
7	24.32	-2.64	41.84	7.23	33.08	2.30
9	-10.64	11.78	64.06	14.49	26.71	13.14

Table 5.4 Percent difference of tetrathionate concentrations between the immediate analysis and the freezing samples without liquid nitrogen (normal freeze) and with liquid nitrogen (fast freeze) at different pHs

pH	First Trial		Second Trial		Average	
	Normal Freeze	Fast Freeze	Normal Freeze	Fast Freeze	Normal Freeze	Fast Freeze
2	-4.19	-31.86	5.04	6.76	0.43	-12.55
4	-5.12	-5.21	29.55	-6.64	12.22	-5.92
7	35.83	2.01	30.91	-0.31	33.37	0.85
9	82.38	1.48	63.48	36.51	72.93	18.99

In general, the difference in concentrations between the immediate analysis and the fast freeze method are lower than the difference in concentrations between the immediate analysis and the normal freeze method. For pH 2, 4, and 7, most of the differences between the fast freeze method and the immediate analysis are in the range of ± 6% for all three thiosalt species studied. However, at pH 9, the differences in concentrations of all three thiosalt species are normally higher than ± 10% for both the normal freeze and fast freeze methods. Although significant variations between the first and the second trial can be seen from Table 5.2, 5.3, and 5.4, the general trends towards greater stability with a fast freeze at pHs between 4 and 7 support the use of the method to preserve speciation until analysis can be done.

Wasserlauf and Dutrizac (1982) reviewed thiosalt stability at pH 3, 4, 7, and 10. Their results illustrated that concentrations of total thiosalt were 7-15% lower than the initial concentrations for the samples that were kept at room temperature; while total thiosalt concentrations were 1-10 % lower than the initial concentrations for the samples that were frozen. Thiosalt concentration significantly decreased in the solution of pH 7 and 10 for the samples that were at room temperature.

The study of Druschel et al. (2003a) on thiosalt stability of trithionate and tetrathionate oxidation by ferric ion (Fe^{3+}) at a pH range of 0.4-2.0 indicated that concentrations of sulphur species during tetrathionate oxidation experiments do not significantly change after storage in a 4°C refrigerator for several days. However, the trithionate oxidation reaction is very fast at lower temperature. Therefore, sample storage in a 4°C refrigerator cannot preserve thiosalt concentrations.

The results obtained from the recent freeze-thaw study are compatible with the results presented in Wasserlauf and Dutrizac (1982) and Druschel et al. (2003a). After sample storage at low temperature, the changes in thiosalt concentration in acidic or neutral solutions are lower than the changes in thiosalt concentrations in a basic solution. Additionally, freezing maintains the stability of thiosalt concentrations.

5.3 Summary

The thiosalt stability study under freeze and thaw conditions in acidic, neutral, and basic solutions was performed. Concentrations of thiosulphate, trithionate, and tetrathionate from the freezing samples without liquid nitrogen (normal freeze) and with liquid nitrogen (fast freeze) were compared with thiosalt concentrations obtained from the immediate analysis.

The results from the freeze-thaw stability study are generally in agreement with the results presented in Wasserlauf and Dutrizac (1982) and Druschel et al., (2003a). The results from the current study illustrate that under acidic and neutral conditions, most of the thiosalt concentration changes were limited to less than ± 6% (with the exception of the tetrathionate at pH 2) after fast freezing in liquid nitrogen, storage in a freezer and thawing in a water bath at 20^{o}C. Therefore, this method may be used to provide a means of storing samples before analysis. Concentrations of thiosalt in acidic and neutral solutions change to a lesser degree than those in a basic solution after storage at low temperature. Moreover, fast freezing seems to be the best approach to maintain the stability of thiosalt concentrations during storage, particularly if analyses cannot be completed immediately after sampling. Further, given the stability of the thiosalt species seems to be best between pHs 4 and 7, it would likely be best to adjust the pH of very acidic or alkaline sample prior to freezing and storage.

CHAPTER 6

THIOSALT KINETIC STUDY

Based on the results obtained from the HSC equilibrium study discussed in Chapter 3 and the results from the freeze-thaw stability study from Chapter 5, kinetic experiments were designed and conducted with the intention of investigating thiosalt reaction kinetics under acidic, neutral, and basic conditions at variable temperatures.

Table 6.1 presents pH and temperature ranges of thiosalt oxidation experiments from previous and current studies. Figure 6.1 displays these conditions graphically. Based on the literature review, most previous studies were performed at high temperatures, specific pH range, or specific thiosalt species. The current study was conduct at lower temperatures, wider pH range and thiosalt species.

Table 6.1 Conditions used in previous and current thiosalt kinetic studies

References	Thiosalt species	pH	Temperature
Xu and Schoonen, 1995	$S_2O_3^{2-}$	2.90-5.20	20°C
Druschel et al., 2003a	$S_4O_6^{2-}$	1.00-2.00	4°C-70°C
Meyer and Ospina, 1982	$S_3O_6^{2-}$, $S_4O_6^{2-}$	3.50-4.00	20°C-70°C
Mizoguchi et al., 1976	$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$	1.95- 7.00	70°C-150°C
Rolia and Chakrabarti, 1982	$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$	5.50-12.00	15°C -85°C
Current study	$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$	2.00, 4.00, 7.00, 9.00	4°C, 15°C, 30°C

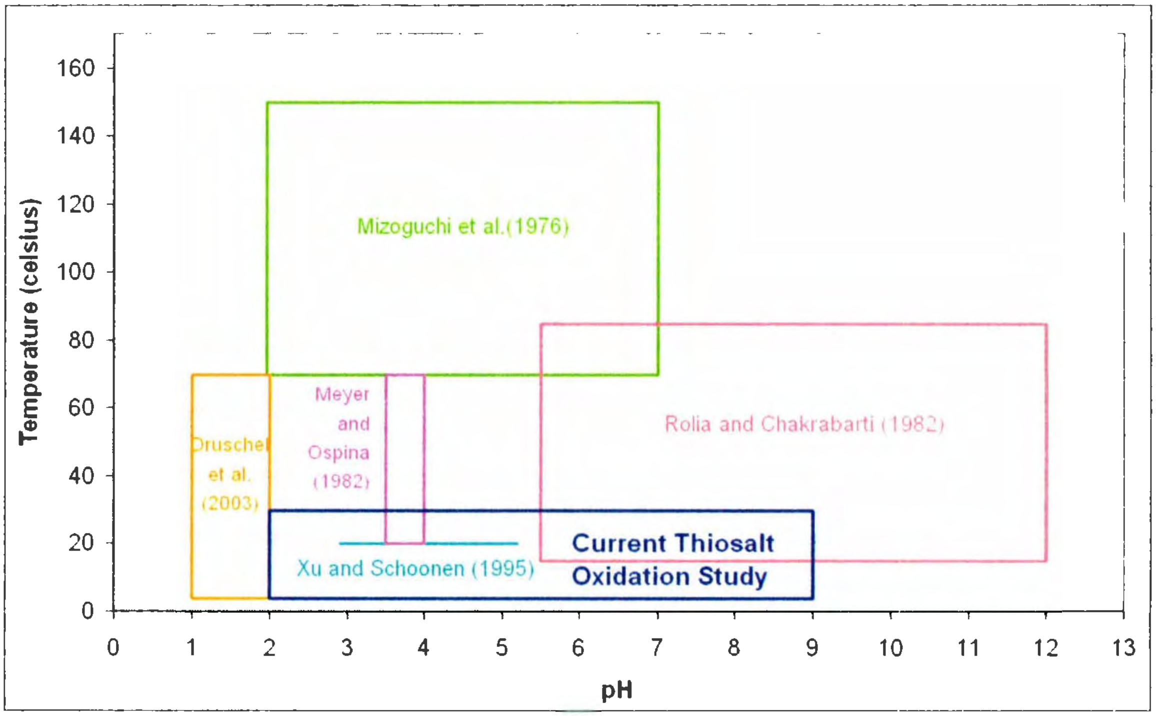

Figure 6.1 Temperature and pH ranges for previous and current thiosalt kinetic studies

6.1 Materials and Method

The thiosalt kinetic study was performed to determine thiosalt behaviour under different pHs and temperatures. Experiments performed involved dissolving thiosalts in buffered or non-buffered solutions with different pHs, storing experimental solutions at designated temperatures, and analyzing the reaction products periodically.

6.1.1 Thiosalt Compounds

The thiosalt compounds utilized in this thiosalt kinetic study were thiosulphate, trithionate, and tetrathionate. The details and synthesis method of these thiosalt species have been described in Chapter 4.

6.1.2 Buffered and Non-buffered Solutions

The pH values of the experimental solutions were 2, 4, 7, and 9. The details of the composition of the experimental solutions used were given in Chapter 5.

6.1.3 Thiosalt and Sulphate Analysis

Thiosalts and sulphate were analyzed using capillary electrophoresis (CE). The method used to analyze thiosalts was modified from O'Reilly et al. (2003) as described in Chapter 4. Sulphate analysis was performed using a CE Forensic Anion Solution Kit purchased from Agilent Technologies. As sulphate cannot be detected by UV-vis, this kit provides indirect detection where a signal is registered if anions that are not UV active displace the UV background electrolyte. The details of the method used for sulphate analysis are as follow (Agilent Technologies, 2000):

- CE: Agilent 1602 capillary electrophoresis equipped with an onboard UV-visible diode-array detector
- Capillary: Agilent Technologies or Simplus brands (MicroSolv Technology Corporation) made of bare fused silica with 50 μm inner diameter, 112.5 cm total length, and 104 cm. effective length
- Background electrolyte: Forensic Anion solution kit buffered with basic pH
    - pH (20°C): 12.10±0.05
    - Conductivity (20°C): 5.2±1.5 mS/cm
    - Source: Agilent Technologies

- CE vial: 1 mL polypropylene vial with polyurethane snap cap, Agilent Technologies
- Injection: Pressure 50 mbar for 6 seconds
- Voltage: 30 kV
- Voltage supply polarity: Negative
- Temperature: 30°C
- Detection wavelength: Signal 350/20 nm
- Reference: 275/10 nm
- Stop Time: 15 minutes

6.1.4 Experimental method

The solutions used in the thiosalt kinetic study were made by dissolving the specific thiosalt compounds in buffer (pH 4, 7, and 9) or acidified deionized water (pH 2) in 100 mL volumetric flasks and making thesolutions up to the mark. Each thiosalt was made in three concentrations (250, 500, and 1000 ppm of the anions) at each pH of interest. The contents of each volumetric flask solution were transferred to a 250 mL volumetric flask sealed with a stopper. The 250 mL flask was filled less than half full (ensure maximal surface area of solution was exposed to air) and placed on a shaker table to maintain a well mixed solution. This solution was saturated with oxygen. The flask was placed in a cooler for experiments at 4°C and an incubator (Innova 4230 refrigerated incubator shaker, New Brunswick Scientific) for experiments at 15°C and 30°C.

Sample aliquots of 1.5 mL were periodically collected and filtered using a syringe with a 0.2 µm nylon filter (17 mm diameter, National Scientific) and transferred to two 1 mL CE vials.

Based on the results obtained from the freeze-thaw stability study, thiosalt concentrations in an alkaline solution change more than ± 10% under freeze-thaw conditions, while the changes are within ±6% for acidic and neutral solution; therefore attempts were made to immediately analyse the sample aliquots of pH 9 experimental solutions. For experimental solutions of pH 2, 4, and 7, the sample vials were fast frozen by liquid nitrogen and stored in a -80°C freezer. Additionally, the dissolved oxygen (DO) concentration and pH of the experimental solutions were measured at the time of sampling.

Before the CE analysis, the sample vials were removed and thawed in a water bath at a temperature of 20°C. The first vial was analysed for thiosalt concentrations. The second vial was analysed for sulphate concentrations.

6.2 Results

Following the experimental method previously described, the concentrations of thiosalt and sulphate were determined as a function of time. The complete detailed experimental results are shown in Appendix C. This section provides an overview and a discussion of these results. Throughout the experimental period, the dissolved oxygen (DO) concentrations of the experimental solutions were in the range of 7.06-10.02 mg/l, the pH of the experimental solutions did not change more than ±0.5 for both buffered and non-buffered solutions, and the temperatures in the cooler and the incubator changed less than ± $2^{o}C$.

6.2.1 Thiosulphate

Thiosulphate decomposition was investigated at temperatures of $4^{o}C$, $15^{o}C$, and $30^{o}C$, and pHs of 2, 4, 7, and 9 with initial thiosulphate concentrations of 250 ppm, 500 ppm, and 1000 ppm in a saturated oxygen condition. The concentrations of thiosulphate, trithionate, tetrathionate, and sulphate were determined as a function of time.

6.2.1.1 pH 2

For experiments at pH 2, thiosulphate rapidly decomposed, especially in the first 24 hours of the experiments. The decomposition products were trithionate, sulphate, and tetrathionate. Figure 6.2 illustrates these changes.

It is important to note that the experimental solutions gradually became cloudy during the first few hours of the experiments and afterwards a yellow precipitate formed. The experimental solutions subsequently became clear.

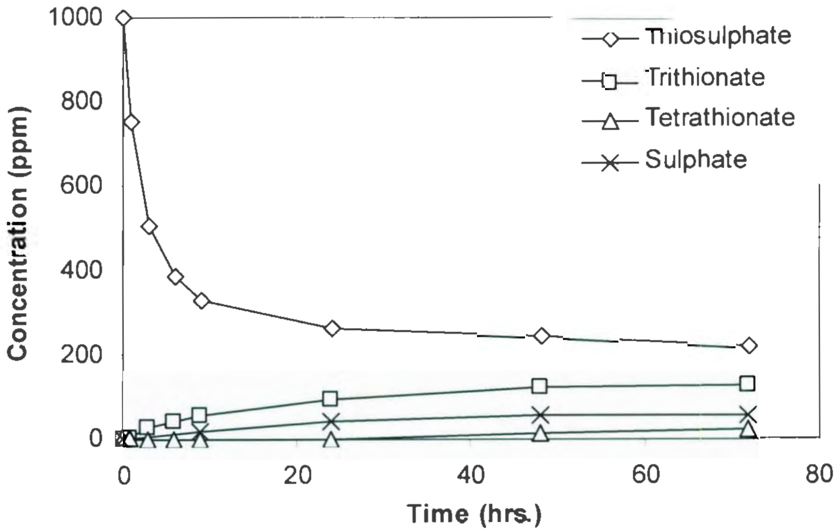

Figure 6.2 Thiosulphate experiments at pH 2 and 30°C

Effect of Initial Thiosulphate Concentration

Table 6.2 presents thiosulphate concentrations as a function of time for pH 2 experiments at 15°C with 250 ppm, 500 ppm, and 1000 ppm initial thiosulphate concentrations. During the experimental period, thiosulphate concentrations decreased by 176 ppm, 359 ppm, and 681 ppm for the experiments with 250 ppm, 500 ppm, and 1000 ppm initial thiosulphate concentrations, respectively. The rate of the thiosulphate reaction was faster as the initial concentration increased as demonstrated by the slope of the curve in Figure 6.3 However, the overall conversion was approximately the same (about 70% thiosulphate decomposition for all three cases). Figure 6.3 illustrates graphically the decrease in thiosulphate concentrations at variable initial thiosulphate concentrations.

Table 6.2 Thiosulphate concentrations for pH 2 experiments at 15°C for varying initial thiosulphate concentrations

Time (hours)	Thiosulphate concentrations		
0	250	500	1000
3	226	422	738
6	201	356	615
9	185	327	540
24	125	213	397
48	98	163	343
72	74	141	319
Final conversion (%)	**70.4**	**71.8**	**68.1**

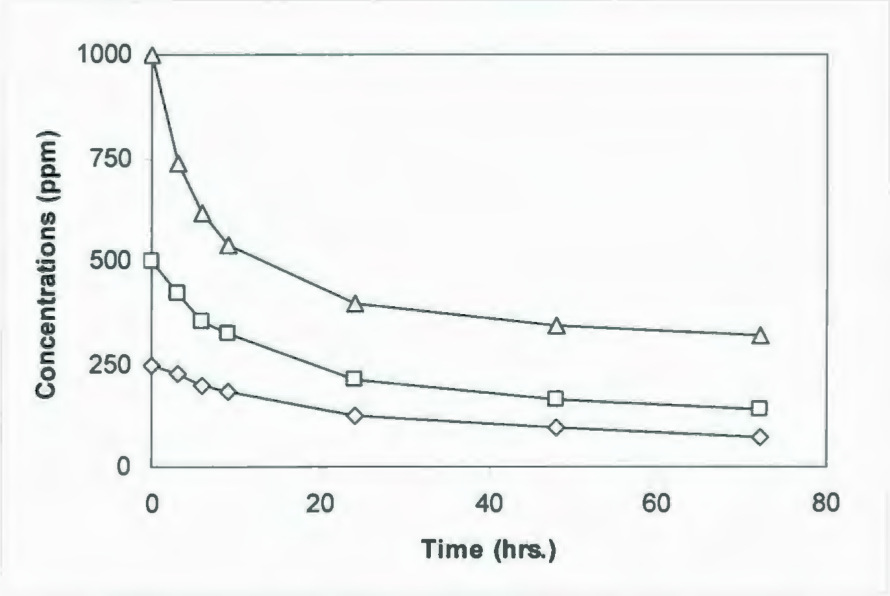

Figure 6.3 Thiosulphate decomposition at pH 2 and 15°C with various initial thiosulphate concentrations

Effect of Temperature

Table 6.3 illustrates the thiosulphate concentrations as a function of time for pH 2 experiments at 4°C, 15°C, and 30°C with the 1000 ppm initial thiosulphate concentration. The final thiosulphate concentrations were 579 ppm, 319 ppm, and 220 ppm for experiments at 4°C, 15°C, and 30°C, respectively. Accordingly, the thiosulphate decomposition rate increased with increasing temperature. The final conversion of thiosulphate was also much lower at the lower temperatures, 42%, 68%, and 78% for experiments at 4°C, 15°C, and 30°C, respectively. Figure 6.4 illustrates graphically the decrease in thiosulphate concentrations at various temperatures.

Table 6.3 Thiosulphate concentrations for pH 2 experiments with varying temperatures

Time (hours)	Thiosulphate Concentration (ppm)		
	4°C	**15°C**	**30°C**
0	1000	1000	1000
3	892	738	507
6	866	615	385
9	816	540	330
24	646	397	262
48	609	343	244
72	579	319	220
Final conversion (%)	**42**	**68**	**78**

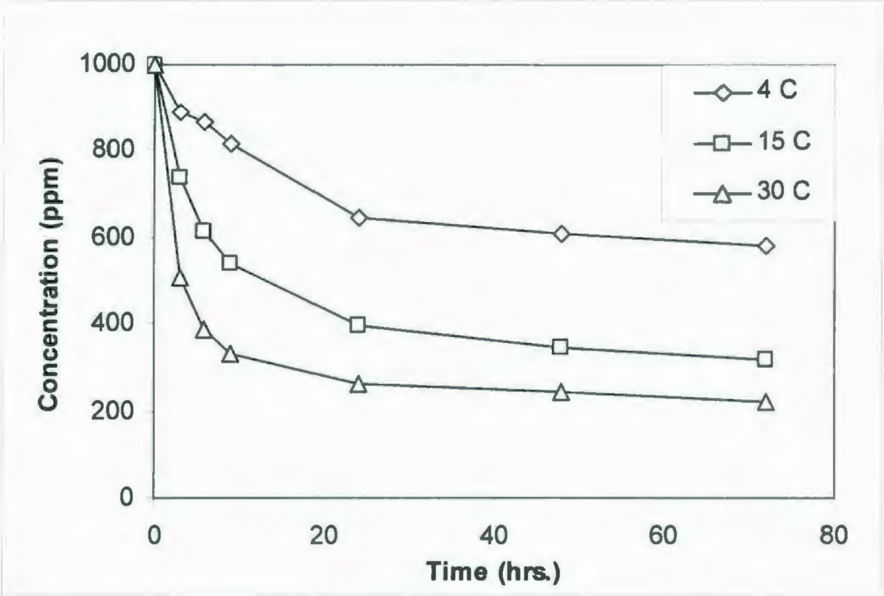

Figure 6.4 Thiosulphate experiments at pH 2 at various temperatures

6.2.1.2 pHs 4 and 7

During the experimental periods, the thiosulphate concentrations decreased less than 5 %. Since the uncertainty in the measurement can be as high as ± 10%, thiosulphate can be considered as fairly stable throughout the experimental period at 4°C-30°C, and 250-1000 ppm initial thiosulphate concentration. However, minute amounts of sulphate, trithionate and tetrathionate were detected.

6.2.1.3 pH 9

For pH 9 experiments at 4°C and 15°C, thiosulphate concentrations decreased less than 6 % during the experimental period. Therefore, under these conditions, thiosulphate is fairly stable. However, trace amounts of trithionate and tetrathionate were detected.

At 30°C, thiosulphate decomposed to trithionate, sulphate, and tetrathionate. Figure 6.5 illustrates the change in concentrations of thiosulphate and the decomposition products formed with time for thiosulphate decomposition at pH 9 and 30°C.

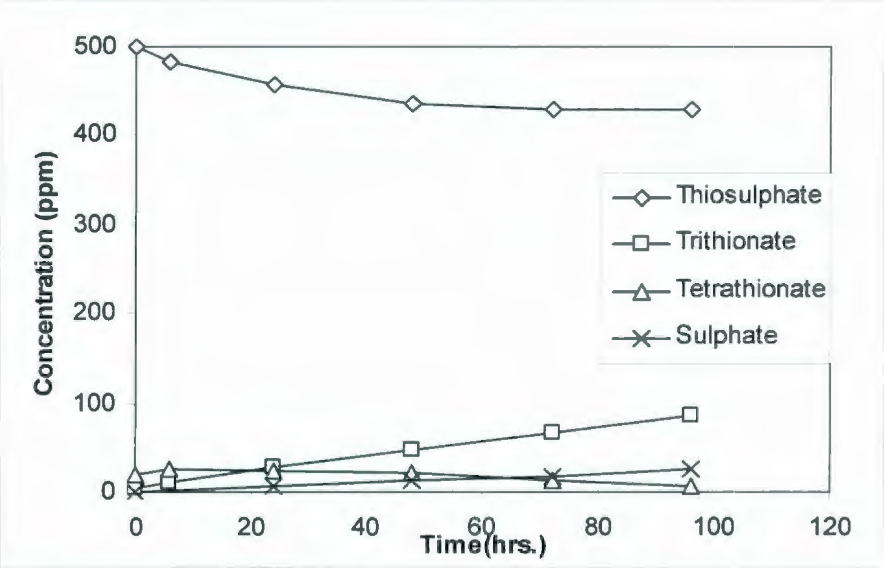

Figure 6.5 Thiosulphate decomposition at pH 9 and 30°C

Effect of Initial Thiosulphate Concentration

Thiosulphate concentrations as a function of time for pH 9 experiments at 15°C with 250 ppm, 500 ppm, and 1000 ppm initial thiosulphate concentrations are shown in Table 6.4. Following the experimental period, thiosulphate concentrations had decreased to 82, 429, and 927 ppm for the experiments with 250 ppm, 500 ppm, and 1000 ppm initial thiosulphate concentrations, respectively. Thiosulphate reacted at a higher rate for the 250 ppm initial concentration as demonstrated in Figure 6.6. The overall conversion is much higher in the lower initial concentration cases as well, with conversions of 67%, 14%, and 7% for the experiments with 250 ppm, 500 ppm, and 1000 ppm initial thiosulphate concentrations, respectively. Figure 6.6 illustrates graphically the decrease in thiosulphate concentrations at different initial thiosulphate concentrations.

Table 6.4 Thiosulphate concentrations for pH 9 experiments at 30°C for varying initial thiosulphate concentrations

Time(hours)	Thiosulphate concentrations (ppm)		
0	250	500	1000
24	192	456	960
48	160	436	960
72	104	429	927
96	82	429	927
Final conversion (%)	**67**	**14**	**7**

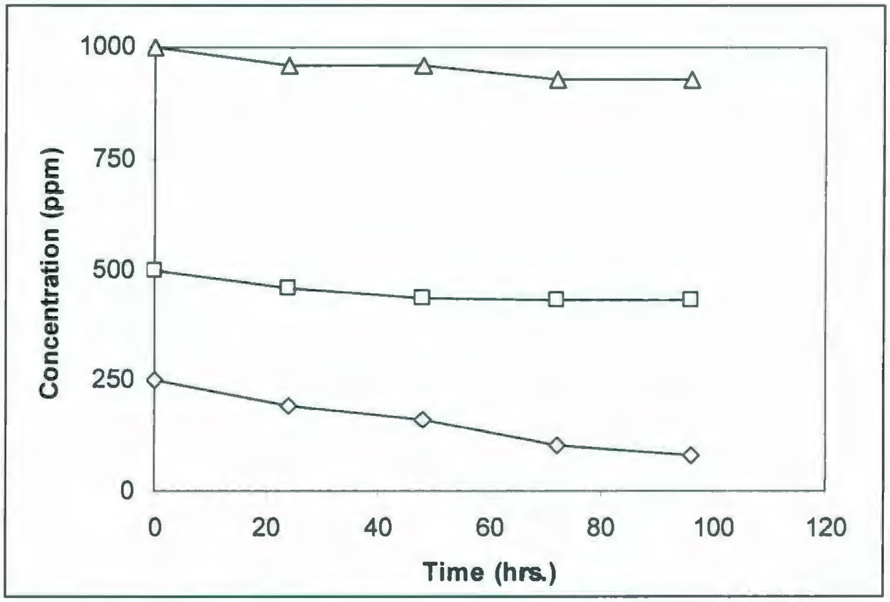

Figure 6.6 Thiosulphate decomposition at pH 9 and 30°C with three initial thiosulphate concentrations

6.2.2 Trithionate

Trithionate decomposition was investigated at temperatures of 4°C, 15°C, and 30°C, and pHs of 2, 4, 7, and 9 with initial trithionate concentrations of 250 ppm, 500 ppm, and 1000 ppm in a saturated oxygen condition. The concentrations of thiosulphate, trithionate, tetrathionate, and sulphate were determined as a function of time.

6.2.2.1 pH 2

For pH 2 experiments at 4°C and 15°C, trithionate concentrations were fairly stable since they decreased within 4%. Nevertheless, sulphate, thiosulphate and tetrathionate were detected in trace amounts.

At 30°C, trithionate decomposed to sulphate, thiosulphate, and tetrathionate. Figure 6.7 illustrates the changes in concentration of trithionate and decomposition products with time for trithionate decomposition at pH 2 and 30°C.

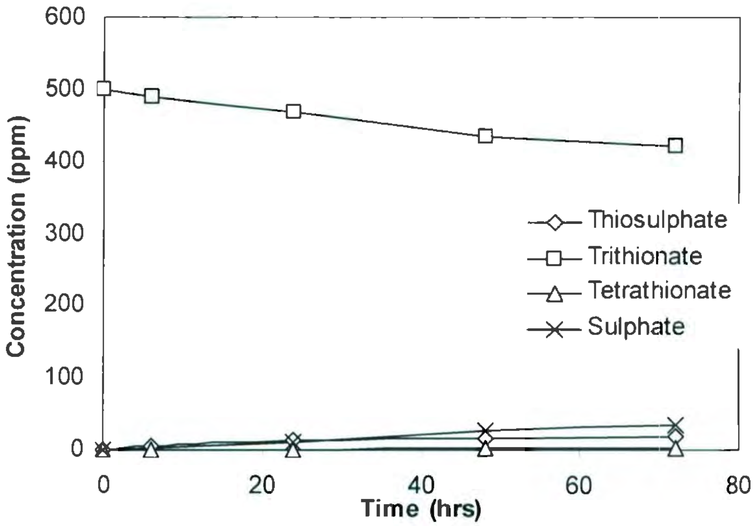

Figure 6.7 Trithionate decomposition at pH 2 and 30°C

Effect of Initial Trithionate Concentration

Trithionate concentrations as a function of time for pH 2 experiments at 30°C with 250 ppm, 500 ppm, and 1000 ppm initial thiosulphate concentrations are shown in Table 6.5. By the end of the experimental period of 72 hours, trithionate concentrations decreased to 209, 419, and 806 ppm for the experiments with 250 ppm, 500 ppm, and 1000 ppm initial trithionate concentrations, respectively. Trithionate decreased faster at higher initial trithionate concentrations; however, the overall relative conversion was approximately the same for all three cases. Figure 6.8 illustrates graphically the decrease in trithionate concentrations for different initial trithionate concentrations.

Table 6.5 Trithionate concentrations for pH 2 experiments at 30°C for varying initial trithionate concentrations

Time (hours)	Trithionate Concentration (ppm)		
0	250	500	1000
6	247	489	930
24	244	468	917
48	233	435	864
72	209	419	806
Final conversion (%)	**16**	**16**	**19**

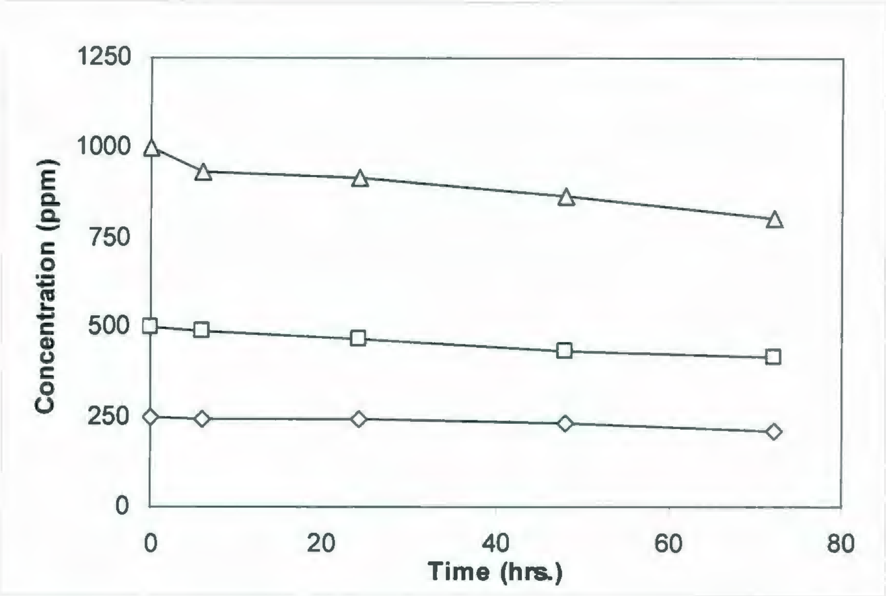

Figure 6.8 Trithionate decomposition at pH 2 and 30°C with various initial trithionate concentrations

6.2.2.2 pH 4

For experiments at pH 4 and 4°C, trithionate concentrations decreased less than 3% within the experimental period. Since the uncertainty in the measurement can be as high as ± 10%, trithionate can be considered as fairly stable under this condition. Though, sulphate and thiosulphate and tetrathionate were detected in trace amounts.

At 15°C and 30°C, trithionate decomposed to sulphate, thiosulphate, and tetrathionate. Figure 6.9 illustrates the changes in concentrations of trithionate and decomposition products formed with time for trithionate decomposition at pH 2 and 30°C. From Figure 6.9, it can be seen that the amounts of sulphate and thiosulphate formed are approximately equivalent.

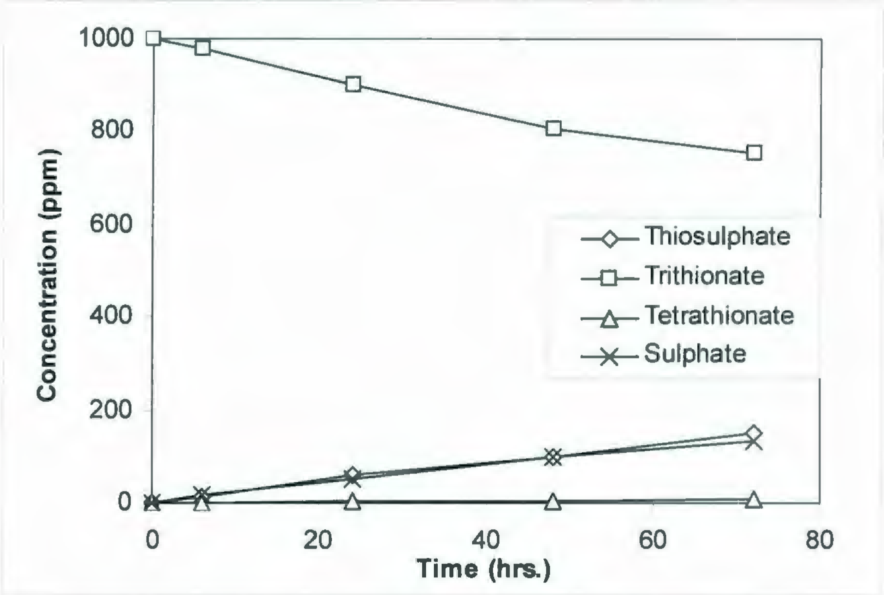

Figure 6.9 Trithionate decomposition at pH 4 and 30°C

Effect of Initial Trithionate Concentration

Trithionate concentrations as a function of time for pH 4 experiments at 30°C with 250 ppm, 500 ppm, and 1000 ppm as initial concentrations of trithionate are shown in Table 6.6. Throughout the experimental period, trithionate concentrations decreased to 189, 379, and 753 ppm for the experiment with 250 ppm, 500 ppm, and 1000 ppm initial concentrations, respectively. Accordingly, trithionate decreases faster at higher initial trithionate concentrations. However, the final degree of conversion is approximately the same regardless of the initial trithionate concentration. Figure 6.10 illustrates graphically the decrease in trithionate concentrations for varying initial trithionate concentrations.

Table 6.6 Trithionate concentrations for pH 4 experiments at 30°C for varying initial trithionate concentrations

Time (hours)	Trithionate Concentration (ppm)		
0	250	500	1000
6	245	481	977
24	222	453	903
48	203	406	806
72	189	379	753
Final conversion (%)	24	24	25

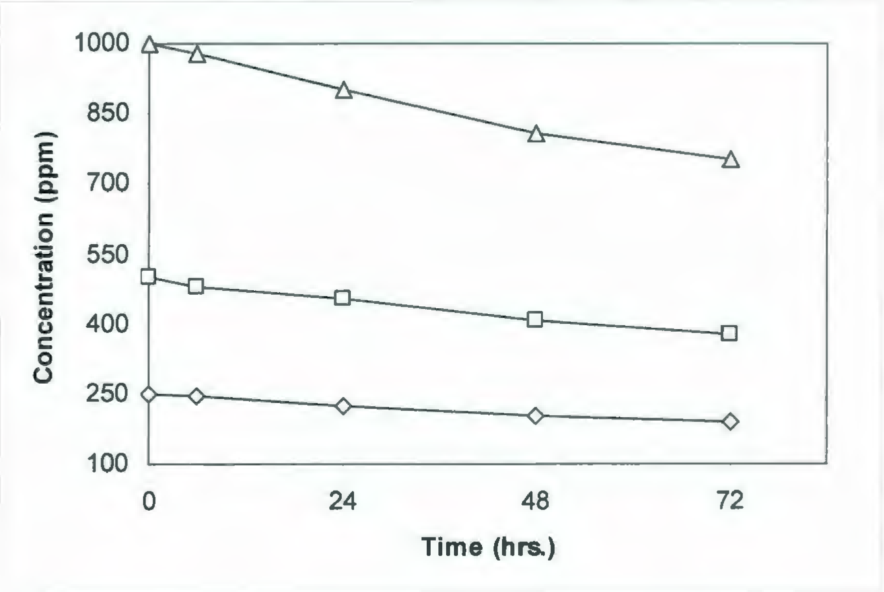

Figure 6.10 Trithionate decomposition at pH 4 and 30°C for various initial trithionate concentrations

Effect of Temperature

Table 6.7 illustrates trithionate concentrations as a function of time for pH 4 experiments at 4°C, 15°C, and 30°C with a 250 ppm initial trithionate concentration. Trithionate concentrations decreased to 244, 229, and 189 ppm for the experiments at 4°C, 15°C, and 30°C, respectively. Therefore, trithionate decomposition rate increases with increasing temperature. Furthermore, trithionate decomposition at 30°C is much faster than at 4°C and 15°C, consequently, the final conversion of trithionate was also significantly higher at the higher temperature. Figure 6.11 illustrates graphically the decreases in trithionate concentrations at various temperatures. The apparent fluctuation in the rate of decomposition seen here, especially at 15°C, can be attributed to the uncertainty in the measurement which can be as high as ±10%.

Table 6.7 Trithionate decomposition at pH 4 at varying temperature

Time (hours)	Trithionate Concentration (ppm)		
	4°C	15°C	30°C
0	250	250	250
24	250	236	222
48	244	239	203
72	244	229	189
Final conversion (%)	**2**	**8**	**24**

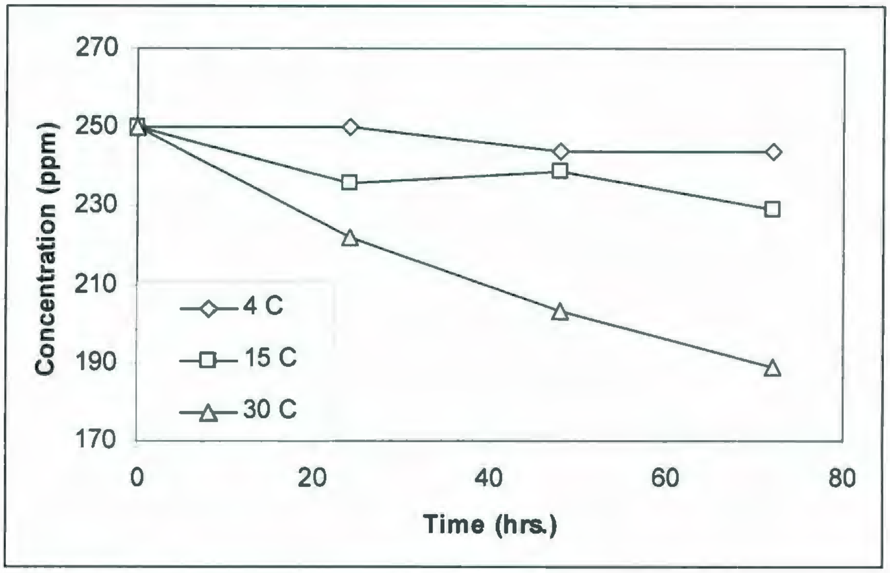

Figure 6.11 Trithionate decompositions at pH 4 at various temperatures

6.2.2.3 pH 7

For pH 7 experiments at 4°C, trithionate concentrations decreased less than 3% within the experimental period. Since the uncertainty in the measurement can be as high as ± 10%, trithionate can be considered as fairly stable under this condition. Nevertheless, trace amounts of thiosulphate and tetrathionate were found.

At 15°C and 30°C, trithionate decomposed primarily to sulphate and thiosulphate, with smaller amounts of tetrathionate. Figure 6.12 demonstrates the typical changes in concentrations of trithionate and decomposition products with time for trithionate decomposition at pH 7 and 30°C. From Figure 6.12, it can be seen that roughly equivalent amounts of sulphate and thiosulphate formed during the course of the experiment.

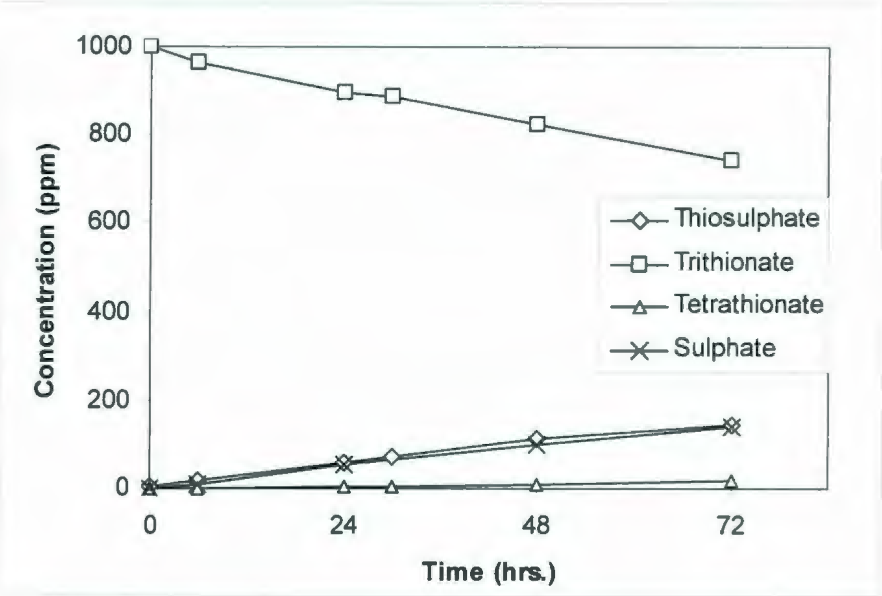

Figure 6.12 Trithionate decomposition at pH 7 and 30°C

Effect of Initial Trithionate Concentration

Trithionate concentrations as a function of time for pH 7 experiments at 30°C with 250 ppm, 500 ppm, and 1000 ppm initial trithionate concentrations are shown in Table 6.8. During the experimental period, trithionate concentrations decreased to 188, 371, and 743 ppm for experiments with 250 ppm, 500 ppm, and 1000 ppm initial trithionate concentrations, respectively. The more rapid reaction of the trithionate at 1000 ppm initial concentration can be seen in Figure 6.13; however, the final conversion is the same regardless of the initial trithionate concentration.

Table 6.8 Trithionate concentrations for pH 7 experiments at 30°C with varying initial trithionate concentrations

Time (hours)	Trithionate Concentration (ppm)		
0	250	500	1000
6	245	491	965
24	237	481	898
48	207	410	825
72	188	371	743
Final conversion (%)	**25**	**26**	**26**

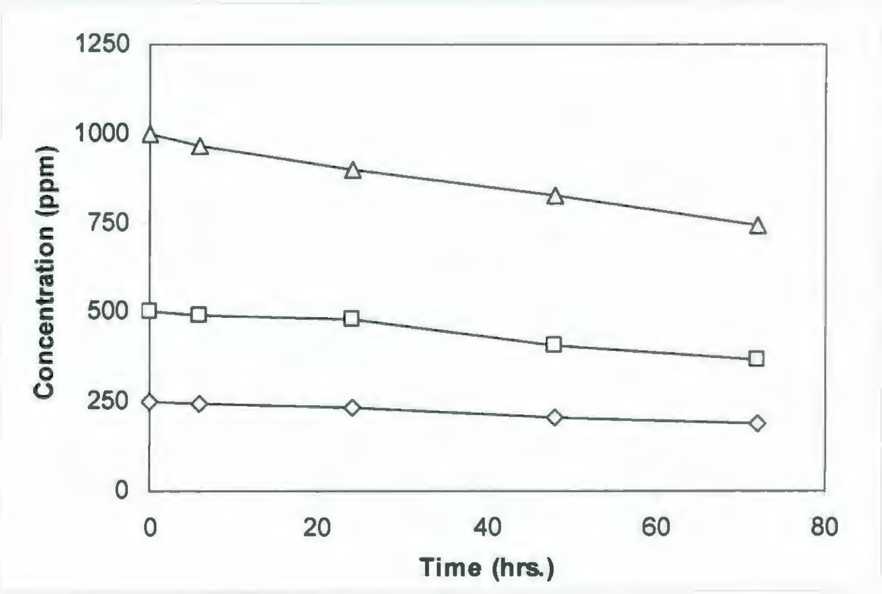

Figure 6.13 Trithionate decomposition at pH 7 and 30°C with various initial trithionate concentrations

Effect of Temperature

Table 6.9 illustrates trithionate concentrations as a function of time for pH 7 experiments at 4°C, 15°C, and 30°C with a 500 ppm initial trithionate concentration. Throughout the experimental period, there was little conversion below 15°C, however at 30°C conversion jumped to 26%. In general, trithionate decomposition rate increases with increasing temperature. Furthermore, trithionate decomposition at 30°C is extreme fast compared to those at 4°C and 15°C, as demonstrated in Figure 6.14.

Table 6.9 Trithionate decomposition at pH 7 for varying temperatures

Time (hours)	Trithionate Concentration (ppm)		
	4°C	15°C	30°C
0	500	500	500
24	500	504	481
48	500	483	410
72	494	471	371
Final conversion (%)	**1**	**6**	**26**

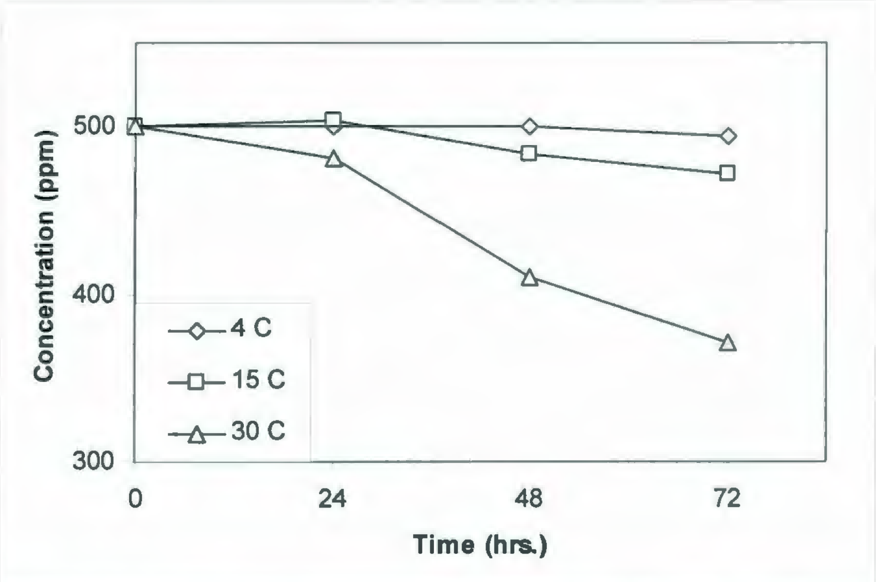

Figure 6.14 Trithionate decompositions at pH 7 at various temperatures

6.2.2.4 pH 9

For pH 9 experiments at 4°C and 15°C, trithionate concentrations decreased within 5 % during the experimental period. Since the uncertainty in the measurement can be as high as ± 10%, trithionate can be considered as fairly stable under this condition. However, small amounts of thiosulphate and tetrathionate were detected.

As with the trithionate decomposition at the lower pHs, the decomposition products are sulphate, thiosulphate, and tetrathionate at 30°C. However here, it can be seen that rather than equal amounts of thiosulphate and sulphate being produced, significantly more sulphate is produced than the other species. Figure 6.15 illustrates the changes in concentrations of trithionate and decomposition products with time for trithionate decomposition at pH 9 and 30°C.

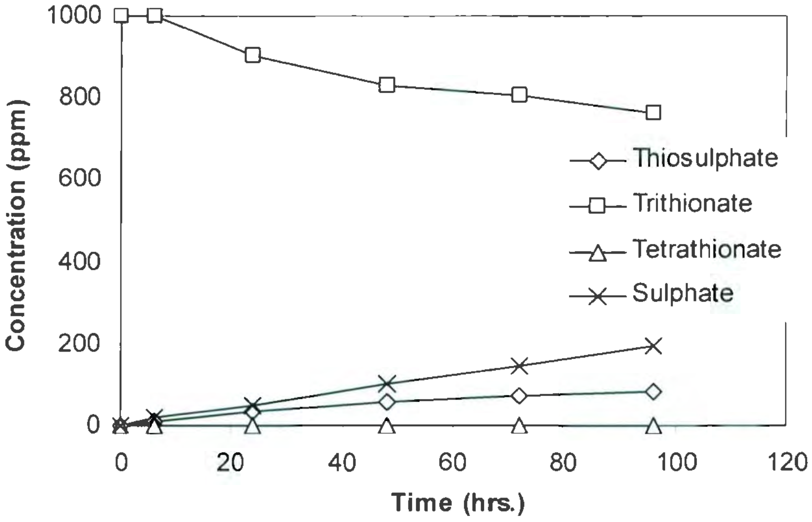

Figure 6.15 Trithionate decomposition at pH 9 and 30°C

Effect of Initial Trithionate Concentration

Change in trithionate concentrations as a function of time for pH 9 experiments at 30°C with 250 ppm, 500 ppm, and 1000 ppm initial trithionate concentrations are shown in Table 6.10. During the 72 hours experiment, trithionate concentrations decreased by 12-14%. Trithionate decreases faster at higher initial trithionate concentrations, though, the final conversions are approximately the same regardless of the initial trithionate concentration. Figure 6.16 illustrates graphically the decrease in trithionate concentrations for different initial trithionate concentrations.

Table 6.10 Trithionate concentrations for pH 9 experiments at 30°C for varying initial trithionate concentrations

Time (hours)	Trithionate Concentration (ppm)		
0	250	500	1000
24	238	494	962
48	234	472	926
72	216	442	858
Final conversion (%)	**14**	**12**	**14**

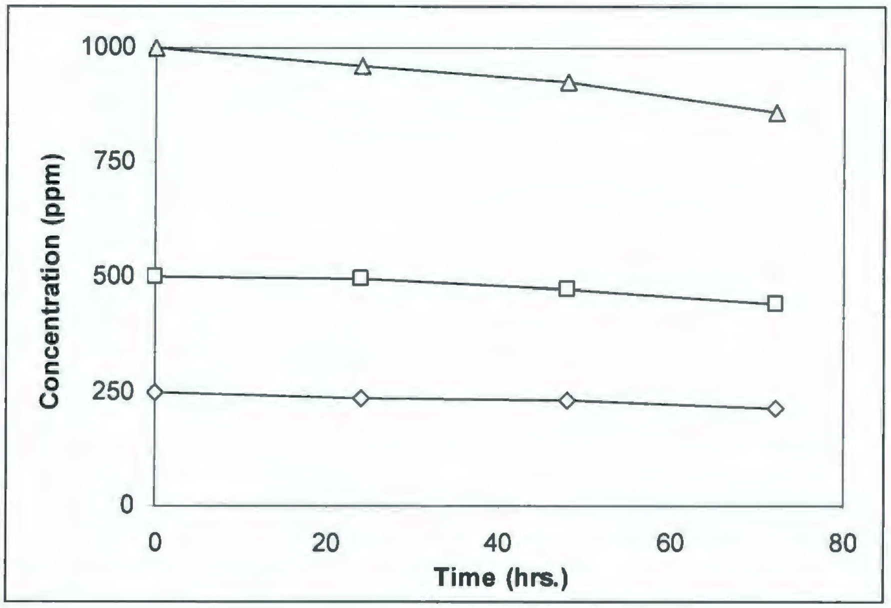

Figure 6.16 Trithionate decomposition at pH 9 and 30°C for various initial trithionate concentrations

6.2.3 Tetrathionate

Tetrathionate decomposition was investigated at temperatures of 4°C, 15°C, and 30°C, and pHs of 2, 4, 7, and 9 with initial tetrathionate concentrations of 250 ppm, 500 ppm, and 1000 ppm in a saturated oxygen condition. The concentrations of thiosulphate, trithionate, tetrathionate, and sulphate were determined as a function of time.

6.2.3.1 pH 2, 4, and 7

During the 72 hours of the experiments at pHs below 7, decreases in tetrathionate concentrations were less than 5 % for all temperatures and initial tetrathionate concentrations. Since the uncertainty in the measurement can be as high as ± 10%, it can be concluded that tetrathionate is fairly stable under the conditions investigated. Neverhteless, minute amounts of trithionate and thiosulphate were detected.

6.2.3.2 pH 9

At pH 9, tetrathionate decomposed to thiosulphate, trithionate, and sulphate. However, in contrast to trithionate, sulphate was not a major product, though thiosulphate was still produced in significant amounts, as was trithionate. Figure 6.17 illustrates the changes in concentrations of tetrathionate and decomposition products with time for the tetrathionate experiment at pH 9 and 30°C.

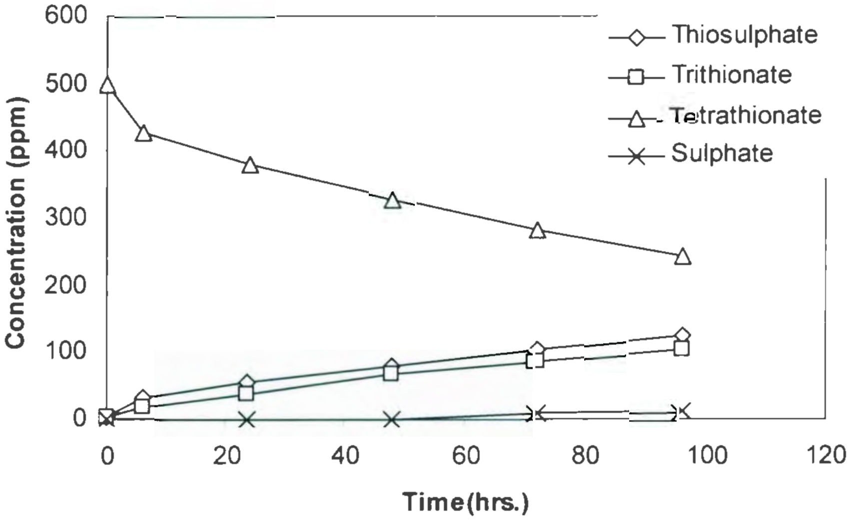

Figure 6.17 Tetrathionate decomposition at pH 9 and 30°C

Effect of Initial Tetrathionate Concentration

Tetrathionate concentrations as a function of time for pH 9 experiments at 30°C with 250 ppm, 500 ppm, and 1000 ppm initial tetrathionate concentrations are shown in Table 6.11. During the experiment, tetrathionate concentrations decreased by 16-44%, with the fastest decreases observed for the two higher initial tetrathionate concentrations. Figure 6.18 illustrates graphically the decreases in tetrathionate concentrations for different initial tetrathionate concentrations.

Table 6.11 Tetrathionate concentrations at pH 9 and 30°C for varying initial tetrathionate concentration

Time (hours)	Tetrathionate Concentration (ppm)		
0	250	500	1000
24	224	381	788
48	222	330	707
72	210	281	599
Final conversion (%)	**16**	**44**	**40**

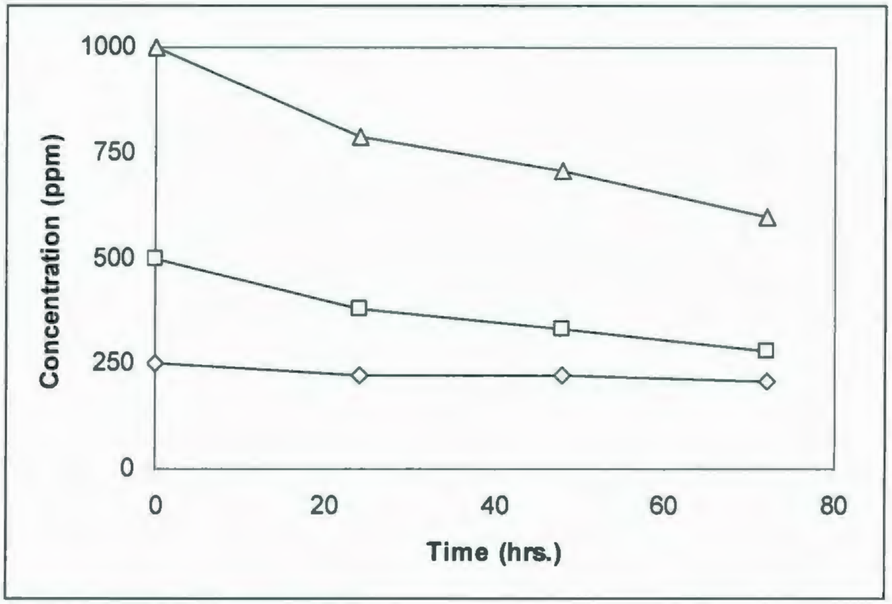

Figure 6.18 Tetrathionate decomposition at pH 9 and 30°C for various initial tetrathionate concentrations

Effect of Temperature

Table 6.12 illustrates tetrathionate concentrations as a function of time for pH 9 experiments at 4°C, 15°C, and 30°C with a 250 ppm initial tetrathionate concentration. Throughout the experimental period, conversion varied from 10-16%. The tetrathionate decomposition rate increased with increasing temperature, showing the fastest decomposition rate at 30°C. Figure 6.19 illustrates graphically the decreases in tetrathionate concentrations at different temperatures.

Table 6.12 Tetrathionate decomposition at pH 9 and varying temperatures

Time (hours)	Tetrathionate Concentration (ppm)		
	4°C	15°C	30°C
0	250	250	250
24	237	238	224
48	227	228	222
72	225	221	210
Final conversion (%)	**10**	**12**	**16**

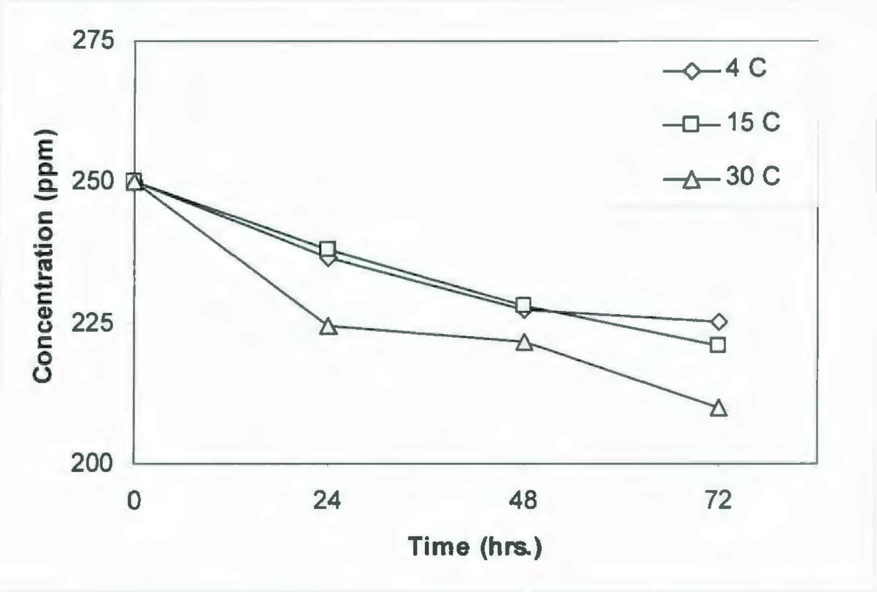

Figure 6.19 Tetrathionate decompositions at pH 9 for various temperatures

6.2.4 Mixture Experiments

The decomposition of a mixture of thiosulphate, trithionate, and tetrathionate was investigated in a saturated oxygen condition with 500 ppm initial concentrations of each thiosalt species.

6.2.4.1 pH 2

At pH 2, thiosulphate concentration decreased by 20-63%, trithionate concentration increased by 3-10% and tetrathionate concentration decreased by 9-14%. In addition, sulphate appeared as a decomposition product. Figure 6.20 illustrates the changes in concentrations of thiosalts and sulphate with time for decomposition of the thiosalt mixture at pH 2 and 15°C.

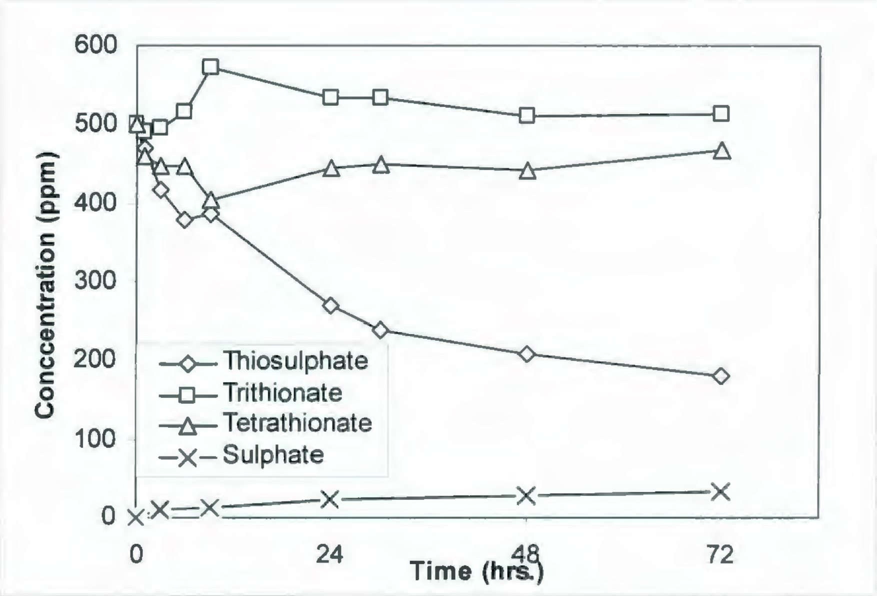

Figure 6.20 Decomposition of a mixture of thiosulphate, trithionate, and tetrathionate at pH 2 and 15°C

6.2.4.2 pH 4

For pH 4 experiments at 4°C, thiosulphate, trithionate and tetrathionate concentrations changes limited to less than 5%; sulphate was detected in small amounts. Since the uncertainty in the measurement can be as high as ± 10%, it can be concluded that thiosalt concentrations are fairly stable under this condition.

At 15°C, thiosulphate and trithionate concentrations changed less than 2% and thus can be considered stable. While tetrathionate concentrations decreased by 10% and sulphate was detected.

At 30°C, thiosulphate concentrations increased by 17% while trithionate and tetrathionate concentrations decreased by 16%. In addition, sulphate was found as a significant decomposition product. Figure 6.21 illustrates the changes in concentrations of thiosalts and sulphate with time for decomposition of the thiosalt mixture at pH 4 and 30°C.

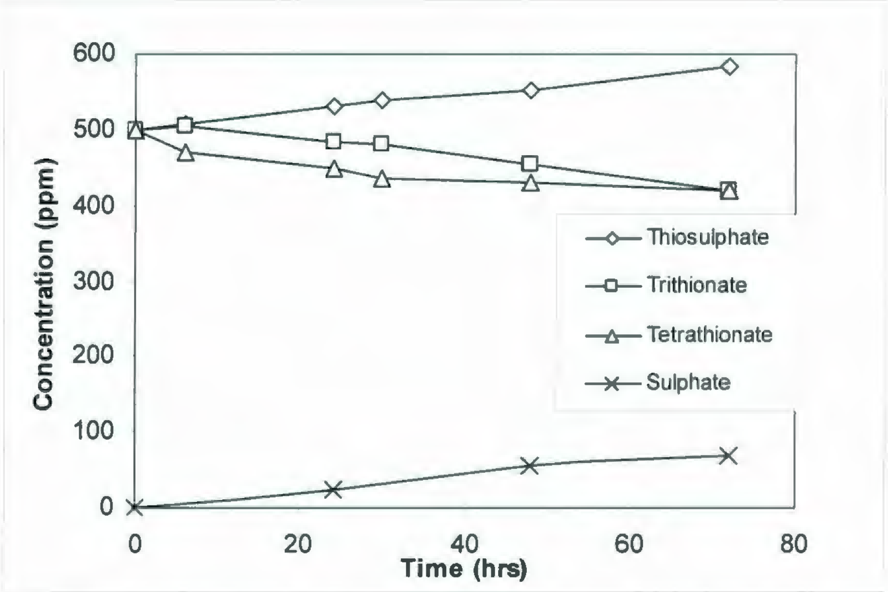

Figure 6.21 Decomposition of a mixture of thiosulphate, trithionate, and tetrathionate at pH 4 and 30°C

6.2.4.3 pH 7

At 4°C, thiosulphate, trithionate, and tetrathionate concentrations were considered to be stable, since their concentrations changed less than 5%, though sulphate was detected. At 15°C, thiosulphate and trithionate concentrations changed less than 2%, while tetrathionate concentrations decreased by 19% and sulphate was detected.

At 30°C, thiosulphate concentrations increased by 18% while trithionate and tetrathionate concentrations decreased by 18% and 20%, respectively. Sulphate was produced as a decomposition product and was measured in increasing amounts as the experiment progressed. Figure 6.22 illustrates the change in concentrations of thiosalts and sulphate with time for the mixture decomposition at pH 7 and 30°C.

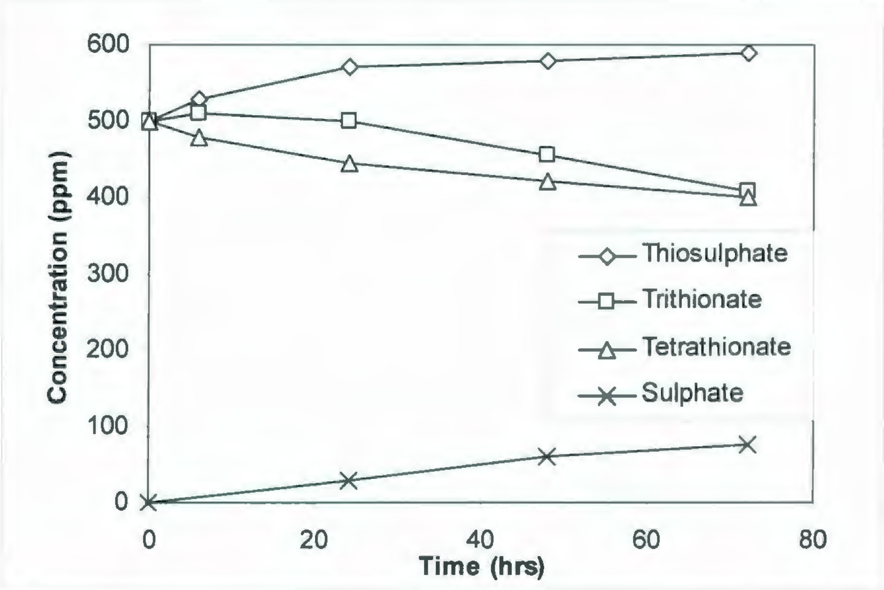

Figure 6.22 Decomposition of a mixture of thiosulphate, trithionate, and tetrathionate at pH 7 and 30°C

6.2.4.4 pH 9

At 4°C and 15°C, thiosulphate and trithionate concentrations increased by 5-7%, while tetrathionate concentrations decreased by 4-11%. In addition, sulphate appeared as a decomposition product.

At 30°C, thiosulphate concentrations increased by 46%, while it was concluded that trithionate concentrations were stable as the concentration decreased by only 5%. Only tetrathionate concentrations decreased substantially (25%). As with the other experiments, sulphate was found as a decomposition product. Figure 6.23 illustrates the change in concentrations of thiosalt and sulphate with time for the mixture decomposition at pH 9 and 30°C.

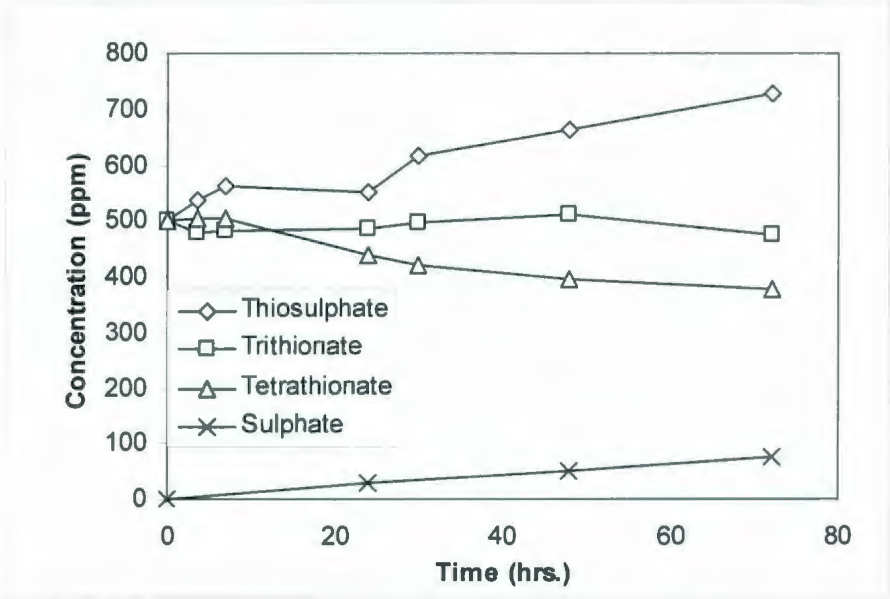

Figure 6.23 Decomposition of a mixture of thiosulphate, trithionate, and tetrathionate at pH 9 and 30°C

6.3 Discussion

6.3.1 Thiosulphate Reaction Kinetics

The results obtained from the thiosulphate kinetic experiments at different pHs and temperatures are summarized in Table 6.13. Thiosulphate concentrations are fairly stable at pHs 4 and 7 within a temperature range of 4^{o}C-30^{o}C. However, at pH 2, thiosulphate decomposes to trithionate, sulphate, and tetrathionate. These results are compatible with the studies of Mizoguchi et al. (1976), Wasserlauf and Dutrizac (1982), and Xu and Schoonen (1995) which proposed the instability of thiosulphate under acidic conditions.

Figure 6.24 compares thiosulphate decomposition between the current study and the study of Xu and Schoonen (1995). The inconsistency between the results of Xu and Schoonen (1995) and the current study presented in Figure 6.24 is possibly because Xu and Schoonen (1995) conducted the experiments at higher pH.

Table 6.13 Thiosulphate stability and decomposition

pH/Temperature	**4^{o}C**	**15^{o}C**	**30^{o}C**
2	Decomposes to $S_3O_6^{2-}$, SO_4^{2-}, $S_4O_6^{2-}$		
4	Stable		
7			
9			Decomposes to $S_3O_6^{2-}$, SO_4^{2-}, $S_4O_6^{2-}$

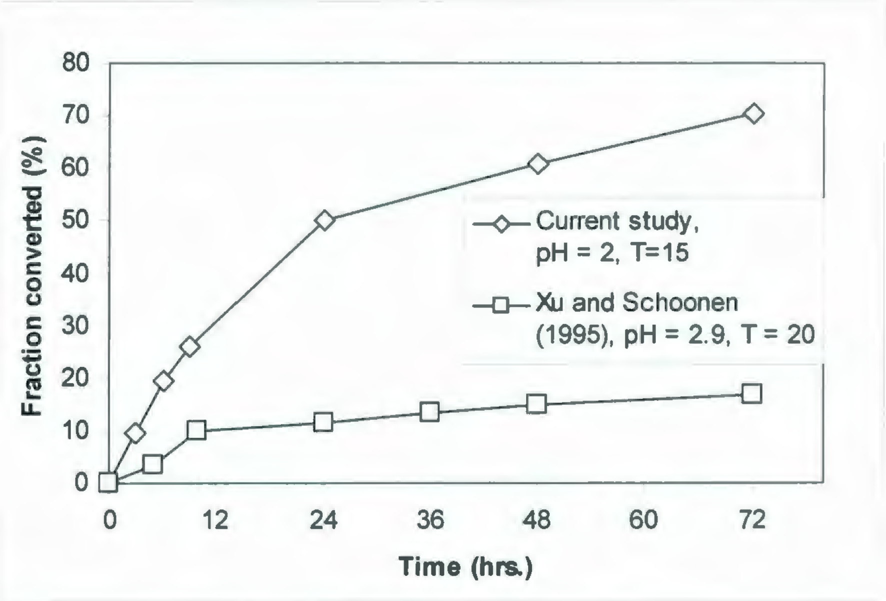

Figure 6.24 Comparison of thiosulphate decomposition between the current study and the study of Xu and Schoonen (1995)
Thiosulphate concentration: Xu and Schoonen (1995), 336 ppm (3000 μM)
Current study, 250 ppm

Furthermore, according to Table 6.2 and 6.3, at pH 2, thiosulphate decomposition rates increased with increasing initial thiosulphate concentration and temperature. The increasing rate with composition indicates a decomposition reaction rate of second or higher order. The degree of conversion seems to be temperature dependent with higher values observed at the higher temperature, and not dependent on initial concentration, where the final conversion was approximately the same regardless of the initial thiosulphate concentration.

For thiosulphate experiments at pH 2, the experimental solutions gradually became cloudy during the first few hours of the experiments. This conforms to the studies of Wasserlauf and Dutrizac (1982) and Xu and Schoonen (1995) which suggested that the experimental solutions were cloudy as a result of the formation of elemental sulphur. Table 6.14 shows the calculated mass balance of sulphur in thiosulphate experiment.

Table 6.14 Mass balance of sulphur for 250 ppm thiosulphate at pH 2 and 4°C

	Initial Concentration (ppm)	Final Concentration (ppm)			
	S in $S_2O_3^{2-}$	S in $S_2O_3^{2-}$	S in $S_3O_6^{2-}$	S in $S_4O_6^{2-}$	S in SO_4^{2-}
	143	90	7	0	6
Total S	**143**	**103**			

The difference between the initial and the final concentration of sulphur is probably due to the elemental sulphur that was formed. The proposing global equation for thiosulphate reaction equilibrium under acidic conditions could be represented by:

$$4S_2O_3^{2-} + 4H^+ \rightarrow S_3O_6^{2-} + SO_4^{2-} + 4S + 2H_2O \qquad (6.1)$$

According to Table 6.13, at pH 9, thiosulphate is stable at 4°C and 15°C; however at 30°C thiosulphate decomposes to trithionate, sulphate, and tetrathionate. Table 6.15 shows the calculated mass balance of sulphur in thiosulphate experiment at pH 9.

Table 6.15 Mass balance of sulphur for 1000 ppm thiosulphate at pH 9 and 30°C

	Initial Concentration (ppm)	Final Concentration (ppm)			
	S in $S_2O_3^{2-}$	S in $S_2O_3^{2-}$	S in $S_3O_6^{2-}$	S in $S_4O_6^{2-}$	S in SO_4^{2-}
	571	529	22	15	3
Total S	**571**	**569**			

The difference between the initial and the final concentration of sulphur can be attributed to the uncertainty in the measurement, which can be as high as ±10%. The proposing global equation for thiosulphate reaction equilibrium at pH 9 may be described by:

$$5S_2O_3^{2-} + 6OH \rightarrow 2S_3O_6^{2-} + S_4O_6^{2-} + 3H_2O \tag{6.2}$$

The difference in mass balance of sulphur between Table 6.14 and 6.15 could be attributed to the formation of elemental sulphur at lower pH. According to Table 6.4, the thiosulphate decomposition rate at 250 ppm initial thiosulphate concentration is faster than at the 500 and 1000 ppm initial thiosulphate concentrations. The final conversion is much higher in the 250 ppm cases as well. Rolia and Chakrabarti (1982) investigated thiosulphate kinetic reactions with oxygen in basic solutions at 75°C -87°C. Their results illustrated that sulphate was produced but tetrathionate was not observed; it was not mentioned whether any attempt was made to measure trithionate.

6.3.2 Trithionate Reaction Kinetics

The results of the trithionate kinetic reaction experiments under different pHs and temperatures are summarized in Table 6.16. At pHs 2 and 9, trithionate is fairly stable at lower temperature (4°C and 15°C), while at 30°C, trithionate decomposes to sulphate, thiosulphate, and tetrathionate. For pHs 4 and 7, the trithionate concentration is stable only at 4°C, while at 15°C and 30°C trithionate decomposes to sulphate, thiosulphate, and tetrathionate. Accordingly, trithionate stability decreases with increasing temperature. Table 6.17 shows the calculated mass balance of sulphur in trithionate experiment at pH 4.

Table 6.16 Trithionate stability and decomposition

<table>
<tr><th>pH/Temperature</th><th>4°C</th><th>15°C</th><th>30°C</th></tr>
<tr><td>2</td><td rowspan="4">Stable</td><td></td><td></td></tr>
<tr><td>4</td><td colspan="2" rowspan="2">Decomposes to SO_4^{2-}, $S_2O_3^{2-}$, $S_4O_6^{2-}$</td></tr>
<tr><td>7</td></tr>
<tr><td>9</td><td></td><td></td></tr>
</table>

Table 6.17 Mass balance of sulphur for 250 ppm trithionate at pH 4 and 15°C

	Initial Concentration (ppm)	Final Concentration (ppm)			
	S in $S_3O_6^{2-}$	S in $S_2O_3^{2-}$	S in $S_3O_6^{2-}$	S in $S_4O_6^{2-}$	S in SO_4^{2-}
	125	3	114	1	5
Total S	**125**	**123**			

The difference between the initial and the final concentration of sulphur can be attributed to the uncertainty in the measurement, which can be as high as ±10%. The proposing global equation for tithionate decomposition under acidic and neutral conditions may be described as follow:

$$S_3O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \tag{6.3}$$

Equation 6.3 is similar to Equations 1.3, 2.10, and 2.20 which were proposed by Wasserlauf and Dutrizac (1982), Mizoguchi et al. (1976), and Rolia and Chakrabarti

(1982), respectively. Table 6.18 shows the calculated mass balance of sulphur in trithionate experiment at pH 9.

Table 6.18 Mass balance of sulphur for 250 ppm trithionate at pH 9 and 30°C

	Initial Concentration (ppm)	Final Concentration (ppm)			
	S in $S_3O_6^{2-}$	S in $S_2O_3^{2-}$	S in $S_3O_6^{2-}$	S in $S_4O_6^{2-}$	S in SO_4^{2-}
	125	9	108	2	14
Total S	**125**	**133**			

The difference between the initial and the final concentration of sulphur can be attributed to the uncertainty in the measurement, which can be as high as ±10%. The proposing global equation for trithionate decomposition reaction under basic conditions could be represented by:

$$S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + H_2O \tag{6.4}$$

The results from the current study are consistent with the studies of Mizoguchi et al. (1976), Wasserlauf and Dutrizac (1982), Meyer and Ospina (1982), and Rolia and Chakrabarti (1982). Figure 6.25 compares trithionate decomposition observed in the current study with the study of Meyer and Ospina (1982). The difference between the results may be attributable to differences in study conditions, where Meyer and Ospina (1982) conducted the experiments using non-buffered solutions at a higher temperature.

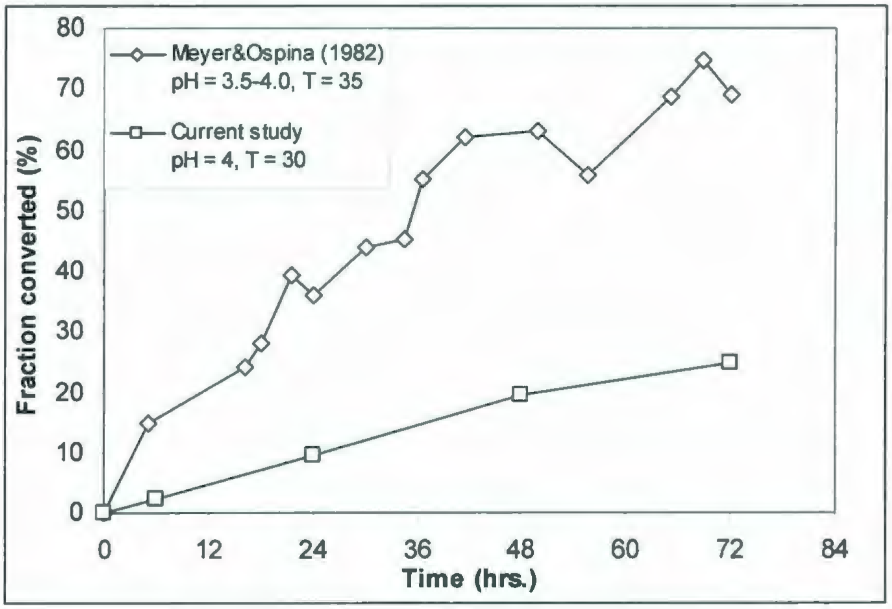

Figure 6.25 Comparison of trithionate decomposition between the current study and the study of Meyer and Ospina (1982)

Trithionate concentration: Meyer and Ospina (1982), 48,048 ppm (0.25 M)

Current study, 1000 ppm

According to Table 6.5 and 6.10, at pHs 2 and 9, trithionate decomposition rates increased with increasing initial trithionate concentration. The increasing rate with composition indicates a decomposition reaction rate of second or higher order. However, the final conversions were approximately the same regardless of the initial thiosulphate concentration suggesting that the mixture of trithionate and decomposition products had reached a steady state and were in equilibrium with each other.

According to Table 6.6, 6.7, 6.8 and 6.9, at pHs 4 and 7, trithionate decomposition rates increased with increasing initial trithionate concentration and temperature. The increasing rate with composition indicates a decomposition reaction rate of second or higher order.

The final conversion was also higher at the higher temperature; while, the final conversion was approximately the same regardless of the initial trithionate concentration.

6.3.3 Tetrathionate Reaction Kinetics

The results of tetrathionate reaction kinetic experiments at different pHs and temperatures are summarized in Table 6.19. At pH 9, tetrathionate decomposed to thiosulphate, trithionate, and sulphate. Table 6.20 shows the calculated mass balance of sulphur in tetrathionate experiment at pH 9.

Table 6.19 Tetrathionate stability and decomposition

pH/Temperature	**4°C**	**15°C**	**30°C**
2	Stable		
4			
7			
9	Decomposes to $S_2O_3^{2-}$, $S_3O_6^{2-}$, SO_4^{2-}		

Table 6.20 Mass balance of sulphur for 500 ppm tetrathionate at pH 9 and 30°C

	Initial Concentration (ppm)	Final Concentration (ppm)			
	S in $S_4O_6^{2-}$	S in $S_2O_3^{2-}$	S in $S_3O_6^{2-}$	S in $S_4O_6^{2-}$	S in SO_4^{2-}
	285	71	52	139	4
Total S	**285**	**266**			

The difference between the initial and the final concentration of sulphur can be attributed to the uncertainty in the measurement, which can be as high as ±10%. The proposing global equation for tetrathionate decomposition reaction under basic conditions could be as illustrated:

$$3S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad (6.5)$$

Equation 6.5 is similar to Equations 2.15 and 2.19 that were proposed by Wasserlauf and Dutrizac and Rolia and Chakrabarti (1982). In general, the results from the current study are compatible with the studies of Wasserlauf and Dutrizac (1982) and Rolia and Chakrabarti (1982).

According to Table 6.11 and 6.12, at pH 9, tetrathionate decomposition rates increased with increasing initial tetrathionate concentration and temperature. The increasing rate with concentration indicates a decomposition reaction rate of second or higher order. The final conversion was also higher at the higher initial tetrathionate concentrations and temperature.

On the other hand, at pHs of 2, 4, and 7 and at 4°C, 15°C, and 30°C, tetrathionate was fairly stable during the experimental period. These results are compatible with the study of Mizoguchi et al. (1976) which proposed that tetrathionate hardly decomposes at temperatures lower than 150°C under acidic conditions.

However, Meyer and Ospina (1982) examined tetrathionate decomposition in non-buffered solutions at pH 3.5-4.0. The results from their study show that, for tetrathionate decomposition at 20°C, thiosulphate and trithionate were noticeable after 140 hours and the solution reached its equilibrium after 26 days. Since the experimental period of the current study was only 72 hours, significant changes in the tetrathionate concentration and the decomposition products similar to the results from Meyer and Ospina (1982) were not detected and cannot be ruled out.

6.3.4 Thiosalt Mixture Reaction Kinetics

The results of the thiosalt mixture kinetic study at different pHs and temperatures are summarized in Table 6.21. At pH 2, the thiosulphate concentrations in a thiosalt mixture solution significantly decrease, forming trithionate and sulphate. The tetrathionate also decomposes to thiosulphate, trithionate and sulphate. This explains the observations that trithionate and sulphate concentrations increase where the other species decrease. In general, trithionate is relatively stable under these conditions; however at pH 4 and greater the trithionate concentration in the thiosalt mixture solution decreased at high temperature. At 4^{o}C, pH 4 and 7, thiosulphate, trithionate, and tetrathionate concentrations were stable. Thiosulphate and trithionate in thiosalt mixture solutions react as in the pure species experiments with reference to the instability of thiosulphate under acidic conditions and trithionate at high temperatures, whereas tetrathionate in thiosalt mixture solutions is more reactive than in pure species experiments as it decomposes at pH $\geq$ 2 in the mixture but decomposes only at pH $\geq$ 9 in the pure species experiments. Table 6.22 shows the calculated mass balance of sulphur in thiosalt mixture at pH 4.

Table 6.21 Thiosalt stability and decomposition in thiosalt mixture experiments

pH/Temperature	4°C	15°C	30°C
2	$S_2O_3^{2-}$ and $S_4O_6^{2-}$ decreased $S_3O_6^{2-}$ increased SO_4^{2-} appeared		
4	$S_2O_3^{2-}$, $S_3O_6^{2-}$,$S_4O_6^{2-}$ stable SO_4^{2-} appeared	$S_2O_3^{2-}$, $S_3O_6^{2-}$ stable $S_4O_6^{2-}$ decreased SO_4^{2-} appeared	$S_2O_3^{2-}$ increased $S_3O_6^{2-}$, $S_4O_6^{2-}$ decreased SO_4^{2-} appeared
7			
9	$S_2O_3^{2-}$, $S_3O_6^{2-}$ increased $S_4O_6^{2-}$ decreased SO_4^{2-} appeared		$S_2O_3^{2-}$ increased $S_3O_6^{2-}$ stable $S_4O_6^{2-}$ decreased SO_4^{2-} appeared

Table 6.22 Mass balance of sulphur in thiosalt mixture at pH 4 and 30°C

	Initial Concentration (ppm)			Final Concentration (ppm)			
	S in $S_2O_3^{2-}$	S in $S_3O_6^{2-}$	S in $S_4O_6^{2-}$	S in $S_2O_3^{2-}$	S in $S_3O_6^{2-}$	S in $S_4O_6^{2-}$	S in SO_4^{2-}
	285	250	285	333	209	239	23
Total S	**820**			**804**			

The difference between the initial and the final concentration of sulphur can be attributed to the uncertainty in the measurement, which can be as high as ±10%. Trithionate decomposition in thiosalt mixture under acidic and neutral conditions may be illustrated by Equation 6.3, while the proposing global equation for tetrathionate decomposition in the thiosalt mixture under these conditions could be represented by:

$$2S_4O_6^{2-} + 3H_2O \leftrightarrow S_2O_3^{2-} + 2S_3O_6^{2-} + 6H^+ \tag{6.6}$$

Under basic conditions, trithionate and tetrathionate decomposition in thiosalt mixture may be described by Equations 6.4 and 6.5, respectively.

6.4 Summary

At pH 2, thiosulphate decomposed to trithionate, sulphate, and tetrathionate. On the other hand, thiosulphate concentrations were fairly stable at pH 4 and 7 in a temperature range of 4^oC-30^oC. At pH 9, thiosulphate concentrations were stable at 4^oC and 15^oC, but decomposed to trithionate, sulphate, and tetrathionate at 30^oC.

At pHs 2 and 9, trithionate was stable at 4^oC and 15^oC, but decomposed to sulphate, thiosulphate and tetrathionate at 30^oC. At pHs 4 and 7, the trithionate concentration was stable at 4^oC, but decomposed to sulphate, thiosulphate and tetrathionate at 15^oC and 30^oC. Accordingly, trithionate stability decreased with increasing temperature.

Tetrathionate was fairly stable at 4^oC, 15^oC, and 30^oC, in solutions of pH 2, 4, and 7 throughout the experimental period. On the contrary, at pH 9, tetrathionate decomposed to thiosulphate, trithionate, and sulphate.

Thiosulphate and trithionate in the thiosalt mixture experiments reacted as in the pure species experiments, while tetrathionate in the thiosalt mixture experiments was more reactive than in the pure species experiments.

Overall, thiosulphate was unstable under acidic conditions, while trithionate was unstable at high temperature and tetrathionate was unstable under basic conditions. However, the conditions in which thiosulphate, trithionate, and tetrathionate concentrations were all stable were at 4^oC in solutions of pH 4 and 7. Moreover, relative rates of decomposition of thiosulphate, trithionate, and tetrathionate are second or higher order.

Thiosalt decomposition rates increased with increasing initial thiosalt concentration and temperature (with the exception of thiosulphate decomposition at pH 9 and 30°C).

This study provided new insights on reactions kinetic of thiosulphate, trithionate, tetrathionate, and the mixture of these thiosalt species at pH and temperature ranges different from the previous studies. These findings are critical to the development of future remediation techniques for mining wastewater.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The main objective of this study was to examine thiosalt behaviour in aqueous media under acidic, neutral and basic conditions in the temperature range that approximated receiving ponds. The thiosalt studies performed in this research were the HSC equilibrium study, the freeze-thaw stability study, and the kinetic reactions study.

Based on the HSC equilibrium study, temperature and pH have strong influences on thiosalt formation. Thiosulphate and polythionate formations were relatively independent of each other under equilibrium conditions. Temperature and initial thiosalt concentrations produced positive effects on thiosalt formation as thiosalt formation was high at high temperature, and high initial thiosalt concentration. On the other hand, pH created a positive effect on thiosulphate formation but a negative effect on polythionate formation. The HSC predictions were based on equilibrium and do not consider reaction kinetics; thus, the equilibrium analysis was simply a tool to aid in the later experimental design.

Capillary Electrophoresis (CE) was used to analyze thiosalt concentrations for the freeze-thaw stability and kinetic studies. The reproducibility of the CE results was in the range of 2-4% for thiosulphate, trithionate, and tetrathionate. Thiosulphate provided the maximum reproducibility, while trithionate showed the minimum value. Coefficients of variation of the thiosalt peak areas obtained from CE analysis were within the range of 6-10%. The peak areas of thiosulphate were the most uniform, while peak areas of tetrathionate were the most variable.

The results from the freeze-thaw stability study illustrated that under acidic and neutral conditions, thiosalt concentration change were limited to less than ± 6% (with the exception of the tetrathionate at pH 2) after fast freezing in liquid nitrogen, storage in a freezer and thawing in a water bath at 20°C. Therefore, this method may be used in further thiosalt studies to provide a means of storing samples before analysis.

According to the thiosalt kinetic reactions study, under acidic conditions, thiosulphate decomposed to trithionate, sulphate, and tetrathionate. Trithionate decomposed to sulphate, thiosulphate and tetrathionate at high temperature. Tetrathionate decomposed to thiosulphate, trithionate, and sulphate under basic conditions. In the thiosalt mixture solutions, thiosulphate and trithionate reacted as in the single species experiments, but tetrathionate was more reactive. In general, the relative rates of decomposition of thiosulphate, trithionate, and tetrathionate were second or higher order. Thiosalt decomposition rates increased with increasing initial thiosalt concentration and temperature (with the exception of thiosulphate decomposition at pH 9 and 30°C).

The HSC equilibrium study and the thiosalt kinetic reactions study provide similar results regarding the strong effects of pH on thiosalt formation and decomposition. However, these studies demonstrated dissimilarity with reference to the relation of thiosulphate and the polythionate, as the results from HSC equilibrium study suggested that thiosulphate and polythionate were relatively independent of each other, whereas the results from the thiosalt kinetic reactions study showed the connections between thiosulphate and the polythionate. Furthermore, with regards to the effects of temperature, the results from the HSC equilibrium proposed the positive effect of temperature on trithionate formation, while the results from the thiosalt kinetic reactions suggested the instability of trithionate at high temperature.

7.2 Future Work

The following recommendations are suggested for augmentation and improvement of the reported works:

1. The results obtained from Chapter 6 can be used to derive kinetic equations for different thiosalt species based on the thiosalt concentration, pH, and temperature. More experiments using a wider range of concentrations, longer experiments and at more pHs and temperatures within the ranges studied herein may be conducted later to fulfill the kinetic equations derivation.

2. Further study on the parameters that have impacts on thiosalt reaction kinetic can be performed with natural catalysts usually presents in acid mine drainage such as ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}).

3. A treatment method and mitigation technology for thiosalt contaminated wastewater can be developed based on the results derived from this study as they proposed the reaction kinetics under different conditions for each thiosalt species.

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APPENDIX A

Results from HSC Chemistry Software

Each table shows the equilibrium composition of thiosalt species and other possible chemical species under different conditions calculated by HSC

Table A.1 Thiosalt 100 ppm , pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	100		
	S4O6(-2a)	100		
	S5O6(-2a)	100		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	275	275	276
	S8(g)	135	134	133
	H2S(a)	0.523	1.19	2.22
	H2SO3(a)	8.1E-07	1.6E-05	2.2E-04
	S2O3(-2a)	2.4E-06	9.4E-06	2.7E-05
	HSO3(-a)	2.8E-07	3.0E-06	2.5E-05
	S4O6(-2a)	8.9E-08	7.9E-07	6.8E-06
	HS(-a)	1.0E-07	6.6E-07	2.4E-06
	SO3(-2a)	2.1E-13	2.0E-12	1.3E-11
	S2O6(-2a)	1.8E-23	2.3E-21	1.9E-19
	S5O6(-2a)	1.5E-22	5.0E-21	1.3E-19
	S3O6(-2a)	1.6E-24	1.6E-22	1.1E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.2 Thiosalt 100 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	100		
	S4O6(-2a)	100		
	S5O6(-2a)	100		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	283	291	303
	S8(g)	124	113	97.6
	H2S(a)	8.95	18.3	30.2
	HS(-a)	1.3E-04	6.5E-04	1.8E-03
	S2O3(-2a)	4.2E-05	1.5E-04	4.1E-04
	HSO3(-a)	6.7E-08	7.6E-07	6.9E-06
	H2SO3(a)	2.7E-09	6.3E-08	1.1E-06
	S4O6(-2a)	3.0E-10	3.2E-09	3.4E-08
	SO3(-2a)	3.7E-12	3.3E-11	1.9E-10
	S2O6(-2a)	6.0E-26	9.6E-24	1.0E-21
	S5O6(-2a)	5.1E-25	2.0E-23	5.9E-22
	S3O6(-2a)	5.3E-27	6.6E-25	5.7E-23
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.3 Thiosulphate 500 ppm , pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	100		
	S4O6(-2a)	100		
	S5O6(-2a)	100		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	503	504	505
	S8(g)	287	287	285
	H2S(a)	0.492	1.12	2.09
	H2SO3(a)	1.2E-06	2.4E-05	3.3E-04
	S2O3(-2a)	4.2E-06	1.6E-05	4.7E-05
	HSO3(-a)	4.2E-07	4.5E-06	3.8E-05
	S4O6(-2a)	2.9E-07	2.6E-06	2.3E-05
	HS(-a)	9.9E-08	6.3E-07	2.3E-06
	SO3(-2a)	3.3E-13	3.2E-12	2.0E-11
	S2O6(-2a)	4.8E-23	6.3E-21	5.3E-19
	S5O6(-2a)	5.6E-22	1.8E-20	4.5E-19
	S3O6(-2a)	4.7E-24	4.8E-22	3.3E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.4 Thiosulphate 500 ppm, pH 8

Table A.2 Thiosalt 100 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	100		
	S4O6(-2a)	100		
	S5O6(-2a)	100		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	562	567	576
	S8(g)	209	202	190
	H2S(a)	62.6	68.6	78.3
	HS(-a)	2.0E-02	2.2E-02	2.3E-02
	S2O3(-2a)	5.9E-04	1.1E-03	2.0E-03
	HSO3(-a)	3.8E-08	5.9E-07	6.4E-06
	H2SO3(a)	6.8E-11	5.6E-09	2.1E-07
	S4O6(-2a)	1.7E-11	6.3E-10	1.4E-08
	SO3(-2a)	4.8E-11	2.3E-10	8.8E-10
	S2O6(-2a)	3.0E-27	1.7E-24	3.7E-22
	S5O6(-2a)	3.1E-26	4.2E-24	2.8E-22
	S3O6(-2a)	2.8E-28	1.2E-25	2.2E-23
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.5 Trithionate 500 ppm , pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	500		
	S4O6(-2a)	100		
	S5O6(-2a)	100		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	608	608	609
	S8(g)	224	223	222
	H2S(a)	0.428	0.973	1.82
	H2SO3(a)	1.5E-06	2.8E-05	4.0E-04
	S2O3(-2a)	4.4E-06	1.7E-05	5.0E-05
	HSO3(-a)	4.8E-07	5.2E-06	4.4E-05
	S4O6(-2a)	4.0E-07	3.5E-06	3.1E-05
	HS(-a)	8.2E-08	5.2E-07	1.9E-06
	SO3(-2a)	3.5E-13	3.4E-12	2.1E-11
	S2O6(-2a)	7.0E-23	9.1E-21	7.6E-19
	S5O6(-2a)	7.4E-22	2.4E-20	6.0E-19
	S3O6(-2a)	6.6E-24	6.8E-22	4.7E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.6 Trithionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	500		
	S4O6(-2a)	100		
	S5O6(-2a)	100		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	611	615	622
	S8(g)	220	214	206
	H2S(a)	3.72	8.27	15.1
	S2O3(-2a)	3.8E-05	1.5E-04	4.2E-04
	HS(-a)	1.8E-05	1.1E-04	3.9E-04
	HSO3(-a)	1.6E-07	1.8E-06	1.5E-05
	H2SO3(a)	2.0E-08	3.9E-07	5.8E-06
	S4O6(-2a)	5.3E-09	4.9E-08	4.4E-07
	SO3(-2a)	3.1E-12	2.9E-11	1.8E-10
	S2O6(-2a)	9.3E-25	1.3E-22	1.1E-20
	S5O6(-2a)	9.7E-24	3.3E-22	8.5E-21
	S3O6(-2a)	8.8E-26	9.4E-24	6.8E-22
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.7 Tetrathionate 500 ppm , pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	100		
	S4O6(-2a)	500		
	S5O6(-2a)	100		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	560	561	562
	S8(g)	268	268	266
	H2S(a)	0.455	1.03	1.94
	H2SO3(a)	1.4E-06	2.7E-05	3.8E-04
	S2O3(-2a)	4.3E-06	1.7E-05	4.8E-05
	HSO3(-a)	4.6E-07	4.9E-06	4.2E-05
	S4O6(-2a)	3.7E-07	3.2E-06	2.8E-05
	HS(-a)	8.7E-08	5.6E-07	2.1E-06
	SO3(-2a)	3.4E-13	3.3E-12	2.0E-11
	S2O6(-2a)	6.1E-23	7.9E-21	6.7E-19
	S5O6(-2a)	6.9E-22	2.2E-20	5.6E-19
	S3O6(-2a)	5.9E-24	6.1E-22	4.2E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.9 Pentathionate 500 ppm , pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	100		
	S4O6(-2a)	100		
	S5O6(-2a)	500		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	525	525	526
	S8(g)	302	301	300
	H2S(a)	0.475	1.08	2.02
	H2SO3(a)	1.3E-06	2.6E-05	3.7E-04
	S2O3(-2a)	4.2E-06	1.6E-05	4.7E-05
	HSO3(-a)	4.4E-07	4.7E-06	4.0E-05
	S4O6(-2a)	3.4E-07	3.0E-06	2.6E-05
	HS(-a)	9.1E-08	5.8E-07	2.2E-06
	SO3(-2a)	3.3E-13	3.2E-12	2.0E-11
	S2O6(-2a)	5.5E-23	7.1E-21	6.0E-19
	S5O6(-2a)	6.5E-22	2.1E-20	5.3E-19
	S3O6(-2a)	5.4E-24	5.5E-22	3.8E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.11 Thiosulphate and trithionate 500 ppm , pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	500		
	S4O6(-2a)	100		
	S5O6(-2a)	100		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	836	837	838
	S8(g)	376	376	375
	H2S(a)	0.426	0.968	1.82
	H2SO3(a)	1.8E-06	3.5E-05	4.9E-04
	S2O3(-2a)	6.0E-06	2.3E-05	6.8E-05
	S4O6(-2a)	7.7E-07	6.8E-06	5.9E-05
	HSO3(-a)	6.0E-07	6.5E-06	5.5E-05
	HS(-a)	8.3E-08	5.3E-07	2.0E-06
	SO3(-2a)	4.5E-13	4.4E-12	2.7E-11
	S2O6(-2a)	1.2E-22	1.5E-20	1.3E-18
	S5O6(-2a)	1.5E-21	4.9E-20	1.2E-18
	S3O6(-2a)	1.2E-23	1.2E-21	8.4E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.8 Tetrathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	100		
	S4O6(-2a)	500		
	S5O6(-2a)	100		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	564	569	576
	S8(g)	264	257	248
	H2S(a)	4.21	9.33	16.9
	HS(-a)	2.3E-05	1.4E-04	4.7E-04
	S2O3(-2a)	4.0E-05	1.5E-04	4.3E-04
	HSO3(-a)	1.5E-07	1.7E-06	1.4E-05
	H2SO3(a)	1.6E-08	3.3E-07	4.9E-06
	S4O6(-2a)	4.3E-09	4.0E-08	3.7E-07
	SO3(-2a)	3.2E-12	3.0E-11	1.8E-10
	S2O6(-2a)	7.2E-25	9.8E-23	8.8E-21
	S5O6(-2a)	8.0E-24	2.7E-22	7.2E-21
	S3O6(-2a)	6.9E-26	7.5E-24	5.5E-22
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.10 Pentathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	100		
	S4O6(-2a)	100		
	S5O6(-2a)	500		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	529	534	541
	S8(g)	296	289	279
	H2S(a)	4.63	10.2	18.4
	HS(-a)	2.7E-05	1.6E-04	5.5E-04
	S2O3(-2a)	4.1E-05	1.6E-04	4.4E-04
	HSO3(-a)	1.4E-07	1.6E-06	1.3E-05
	H2SO3(a)	1.4E-08	2.9E-07	4.3E-06
	S4O6(-2a)	3.6E-09	3.3E-08	3.1E-07
	SO3(-2a)	3.2E-12	3.0E-11	1.9E-10
	S2O6(-2a)	5.8E-25	8.0E-23	7.3E-21
	S5O6(-2a)	6.8E-24	2.3E-22	6.2E-21
	S3O6(-2a)	5.7E-26	6.2E-24	4.6E-22
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.12 Thiosulphate and trithionate 500 ppm , pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	500		
	S4O6(-2a)	100		
	S5O6(-2a)	100		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	842	849	858
	S8(g)	369	360	347
	H2S(a)	6.4	13.7	23.9
	HS(-a)	7.3E-05	4.1E-04	1.3E-03
	S2O3(-2a)	9.1E-05	3.3E-04	9.1E-04
	HSO3(-a)	1.6E-07	1.7E-06	1.5E-05
	H2SO3(a)	7.9E-09	1.7E-07	2.8E-06
	S4O6(-2a)	3.4E-09	3.4E-08	3.4E-07
	SO3(-2a)	6.9E-12	6.3E-11	3.7E-10
	S2O6(-2a)	5.2E-25	7.6E-23	7.5E-21
	S5O6(-2a)	6.6E-24	2.4E-22	6.9E-21
	S3O6(-2a)	5.3E-26	6.1E-24	4.8E-22
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.13 Thiosulphate and tetrathionate 500 ppm , pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	100		
	S4O6(-2a)	500		
	S5O6(-2a)	100		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	789	789	790
	S8(g)	421	420	419
	H2S(a)	0.443	1.01	1.89
	H2SO3(a)	1.7E-06	3.3E-05	4.7E-04
	S2O3(-2a)	5.9E-06	2.3E-05	6.7E-05
	S4O6(-2a)	7.2E-07	6.3E-06	5.5E-05
	HSO3(-a)	5.8E-07	6.3E-06	5.3E-05
	HS(-a)	8.7E-08	5.6E-07	2.1E-06
	SO3(-2a)	4.4E-13	4.2E-12	2.6E-11
	S2O6(-2a)	1.1E-22	1.4E-20	1.2E-18
	S5O6(-2a)	1.4E-21	4.6E-20	1.2E-18
	S3O6(-2a)	1.1E-23	1.1E-21	7.7E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.14 Thiosulphate and tetrathionate 500 ppm , pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	100		
	S4O6(-2a)	500		
	S5O6(-2a)	100		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	796	804	814
	S8(g)	412	401	387
	H2S(a)	7.79	16.3	27.7
	HS(-a)	1.1E-04	5.9E-04	1.7E-03
	S2O3(-2a)	1.0E-04	3.8E-04	1.0E-03
	HSO3(-a)	1.4E-07	1.6E-06	1.4E-05
	H2SO3(a)	5.6E-09	1.3E-07	2.2E-06
	S4O6(-2a)	2.3E-09	2.4E-08	2.5E-07
	SO3(-2a)	7.8E-12	7.0E-11	4.0E-10
	S2O6(-2a)	3.5E-25	5.3E-23	5.5E-21
	S5O6(-2a)	4.6E-24	1.7E-22	5.3E-21
	S3O6(-2a)	3.5E-26	4.3E-24	3.6E-22
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.15 Trithionate and tetrathionate 500 ppm, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	500		
	S4O6(-2a)	500		
	S5O6(-2a)	100		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	893	894	895
	S8(g)	357	357	356
	H2S(a)	0.401	0.91	1.71
	H2SO3(a)	2.0E-06	3.9E-05	5.4E-04
	S4O6(-2a)	9.0E-07	7.9E-06	6.9E-05
	S2O3(-2a)	6.0E-06	2.3E-05	6.8E-05
	HSO3(-a)	6.4E-07	6.9E-06	5.8E-05
	HS(-a)	7.5E-08	4.8E-07	1.8E-06
	SO3(-2a)	4.6E-13	4.4E-12	2.8E-11
	S2O6(-2a)	1.4E-22	1.8E-20	1.5E-18
	S5O6(-2a)	1.8E-21	5.7E-20	1.4E-18
	S3O6(-2a)	1.4E-23	1.4E-21	9.9E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.16 Trithionate and tetrathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	500		
	S4O6(-2a)	500		
	S5O6(-2a)	100		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	896	899	903
	S8(g)	355	350	344
	H2S(a)	2.61	5.87	10.9
	S2O3(-2a)	3.9E-05	1.5E-04	4.4E-04
	HS(-a)	8.0E-06	5.1E-05	1.8E-04
	HSO3(-a)	2.5E-07	2.7E-06	2.3E-05
	H2SO3(a)	4.7E-08	9.3E-07	1.3E-05
	S4O6(-2a)	2.1E-08	1.9E-07	1.7E-06
	SO3(-2a)	3.0E-12	2.9E-11	1.8E-10
	S2O6(-2a)	3.3E-24	4.4E-22	3.8E-20
	S5O6(-2a)	4.1E-23	1.4E-21	3.5E-20
	S3O6(-2a)	3.3E-25	3.5E-23	2.4E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.17 Thiosulphate, tri- and tetrathionate 500 ppm, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	500		
	S4O6(-2a)	500		
	S5O6(-2a)	100		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1120	1120	1120
	S8(g)	510	509	508
	H2S(a)	0.399	0.908	1.7
	H2SO3(a)	2.3E-06	4.4E-05	6.2E-04
	S4O6(-2a)	1.4E-06	1.3E-05	1.1E-04
	S2O3(-2a)	7.5E-06	2.9E-05	8.5E-05
	HSO3(-a)	7.5E-07	8.0E-06	6.8E-05
	HS(-a)	7.6E-08	4.9E-07	1.8E-06
	SO3(-2a)	5.5E-13	5.3E-12	3.3E-11
	S5O6(-2a)	2.9E-21	9.3E-20	2.3E-18
	S2O6(-2a)	2.0E-22	2.6E-20	2.2E-18
	S3O6(-2a)	2.1E-23	2.2E-21	1.5E-19
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.18 Thiosulphate, tri- and tetrathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	500		
	S4O6(-2a)	500		
	S5O6(-2a)	100		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1120	1130	1130
	S8(g)	506	501	492
	H2S(a)	3.47	7.77	14.2
	S2O3(-2a)	6.6E-05	2.5E-04	7.2E-04
	HS(-a)	1.7E-05	1.1E-04	3.7E-04
	HSO3(-a)	2.5E-07	2.8E-06	2.4E-05
	H2SO3(a)	3.0E-08	6.0E-07	8.9E-06
	S4O6(-2a)	1.9E-08	1.7E-07	1.6E-06
	SO3(-2a)	4.8E-12	4.6E-11	2.8E-10
	S5O6(-2a)	3.8E-23	1.3E-21	3.3E-20
	S2O6(-2a)	2.7E-24	3.6E-22	3.2E-20
	S3O6(-2a)	2.8E-25	3.0E-23	2.1E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.19 Thiosulphate and pentathionate 500 ppm, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	100		
	S4O6(-2a)	100		
	S5O6(-2a)	500		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	753	754	754
	S8(g)	454	453	452
	H2S(a)	0.457	1.04	1.95
	H2SO3(a)	1.7E-06	3.2E-05	4.6E-04
	S2O3(-2a)	5.8E-06	2.3E-05	6.5E-05
	S4O6(-2a)	6.8E-07	6.0E-06	5.2E-05
	HSO3(-a)	5.7E-07	6.1E-06	5.1E-05
	HS(-a)	9.0E-08	5.8E-07	2.1E-06
	SO3(-2a)	4.3E-13	4.1E-12	2.6E-11
	S5O6(-2a)	1.4E-21	4.4E-20	1.1E-18
	S2O6(-2a)	9.9E-23	1.3E-20	1.1E-18
	S3O6(-2a)	1.0E-23	1.1E-21	7.2E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.20 Thiosulphate and pentathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	100		
	S4O6(-2a)	100		
	S5O6(-2a)	500		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	761	770	782
	S8(g)	443	431	416
	H2S(a)	9.26	18.8	31.1
	HS(-a)	1.7E-04	8.2E-04	2.2E-03
	S2O3(-2a)	1.2E-04	4.2E-04	1.1E-03
	HSO3(-a)	1.3E-07	1.4E-06	1.3E-05
	H2SO3(a)	4.1E-09	9.8E-08	1.8E-06
	S4O6(-2a)	1.6E-09	1.8E-08	2.0E-07
	SO3(-2a)	8.8E-12	7.7E-11	4.3E-10
	S2O6(-2a)	2.4E-25	3.9E-23	4.3E-21
	S5O6(-2a)	3.3E-24	1.3E-22	4.2E-21
	S3O6(-2a)	2.5E-26	3.2E-24	2.8E-22
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.21 Trithionate and pentathionate 500 ppm, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	500		
	S4O6(-2a)	100		
	S5O6(-2a)	500		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	858	858	859
	S8(g)	391	390	389
	H2S(a)	0.413	0.938	1.76
	H2SO3(a)	1.9E-06	3.8E-05	5.3E-04
	S2O3(-2a)	6.0E-06	2.3E-05	6.7E-05
	S4O6(-2a)	8.6E-07	7.6E-06	6.6E-05
	HSO3(-a)	6.2E-07	6.7E-06	5.7E-05
	HS(-a)	7.7E-08	5.0E-07	1.8E-06
	SO3(-2a)	4.5E-13	4.3E-12	2.7E-11
	S2O6(-2a)	1.3E-22	1.7E-20	1.4E-18
	S5O6(-2a)	1.7E-21	5.5E-20	1.4E-18
	S3O6(-2a)	1.3E-23	1.4E-21	9.3E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.22 Trithionate and pentathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	500		
	S4O6(-2a)	100		
	S5O6(-2a)	500		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	860	863	868
	S8(g)	388	383	377
	H2S(a)	2.77	6.22	11.5
	S2O3(-2a)	4.0E-05	1.5E-04	4.4E-04
	HS(-a)	8.9E-06	5.6E-05	2.0E-04
	HSO3(-a)	2.4E-07	2.6E-06	2.2E-05
	H2SO3(a)	4.3E-08	8.5E-07	1.2E-05
	S4O6(-2a)	1.9E-08	1.7E-07	1.5E-06
	SO3(-2a)	3.0E-12	2.9E-11	1.8E-10
	S2O6(-2a)	2.9E-24	3.9E-22	3.3E-20
	S5O6(-2a)	3.8E-23	1.2E-21	3.2E-20
	S3O6(-2a)	3.0E-25	3.1E-23	2.2E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.23 Thiosulphate,tri- and pentathionate 500 ppm, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	500		
	S4O6(-2a)	100		
	S5O6(-2a)	500		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1090	1090	1090
	S8(g)	543	543	542
	H2S(a)	0.409	0.929	1.74
	H2SO3(a)	2.2E-06	4.3E-05	6.1E-04
	S4O6(-2a)	1.4E-06	1.2E-05	1.0E-04
	S2O3(-2a)	7.5E-06	2.9E-05	8.4E-05
	HSO3(-a)	7.3E-07	7.9E-06	6.7E-05
	HS(-a)	7.8E-08	5.0E-07	1.9E-06
	SO3(-2a)	5.4E-13	5.2E-12	3.3E-11
	S5O6(-2a)	2.8E-21	9.0E-20	2.3E-18
	S2O6(-2a)	1.9E-22	2.5E-20	2.1E-18
	S3O6(-2a)	2.0E-23	2.1E-21	1.4E-19
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.24 Thiosulphate,tri- and pentathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	500		
	S4O6(-2a)	100		
	S5O6(-2a)	500		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1090	1090	1100
	S8(g)	539	533	525
	H2S(a)	3.73	8.32	15.2
	S2O3(-2a)	6.8E-05	2.6E-04	7.4E-04
	HS(-a)	2.0E-05	1.2E-04	4.2E-04
	HSO3(-a)	2.4E-07	2.6E-06	2.3E-05
	H2SO3(a)	2.7E-08	5.4E-07	8.0E-06
	S4O6(-2a)	1.6E-08	1.5E-07	1.4E-06
	SO3(-2a)	4.9E-12	4.7E-11	2.9E-10
	S5O6(-2a)	3.3E-23	1.1E-21	3.0E-20
	S2O6(-2a)	2.3E-24	3.1E-22	2.7E-20
	S3O6(-2a)	2.4E-25	2.6E-23	1.9E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.25 Tetra- and pentathionate 500 ppm, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	100		
	S4O6(-2a)	500		
	S5O6(-2a)	500		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	810	811	811
	S8(g)	435	434	433
	H2S(a)	0.429	0.975	1.83
	H2SO3(a)	1.9E-06	3.6E-05	5.1E-04
	S2O3(-2a)	5.9E-06	2.3E-05	6.6E-05
	S4O6(-2a)	8.0E-07	7.1E-06	6.2E-05
	HSO3(-a)	6.0E-07	6.5E-06	5.5E-05
	HS(-a)	8.0E-08	5.2E-07	1.9E-06
	SO3(-2a)	4.4E-13	4.2E-12	2.6E-11
	S5O6(-2a)	1.6E-21	5.2E-20	1.3E-18
	S2O6(-2a)	1.2E-22	1.5E-20	1.3E-18
	S3O6(-2a)	1.2E-23	1.3E-21	8.6E-20
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.26 Tetra- and pentathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	100		
	S4O6(-2a)	500		
	S5O6(-2a)	500		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	813	816	821
	S8(g)	432	427	420
	H2S(a)	3	6.74	12.4
	S2O3(-2a)	4.1E-05	1.6E-04	4.5E-04
	HS(-a)	1.0E-05	6.5E-05	2.3E-04
	HSO3(-a)	2.3E-07	2.5E-06	2.1E-05
	H2SO3(a)	3.8E-08	7.6E-07	1.1E-05
	S4O6(-2a)	1.7E-08	1.5E-07	1.3E-06
	SO3(-2a)	3.1E-12	2.9E-11	1.8E-10
	S2O6(-2a)	2.4E-24	3.2E-22	2.8E-20
	S5O6(-2a)	3.3E-23	1.1E-21	2.8E-20
	S3O6(-2a)	2.5E-25	2.6E-23	1.9E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.27 Thiosulphate, tetra- and pentathionate 500 ppm, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	100		
	S4O6(-2a)	500		
	S5O6(-2a)	500		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1040	1040	1040
	S8(g)	588	587	586
	H2S(a)	0.421	0.957	1.8
	H2SO3(a)	2.2E-06	4.2E-05	5.9E-04
	S4O6(-2a)	1.3E-06	1.1E-05	9.8E-05
	S2O3(-2a)	7.4E-06	2.9E-05	8.3E-05
	HSO3(-a)	7.1E-07	7.7E-06	6.5E-05
	HS(-a)	8.1E-08	5.2E-07	1.9E-06
	SO3(-2a)	5.3E-13	5.1E-12	3.2E-11
	S5O6(-2a)	2.7E-21	8.6E-20	2.2E-18
	S2O6(-2a)	1.8E-22	2.3E-20	1.9E-18
	S3O6(-2a)	1.9E-23	1.9E-21	1.3E-19
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.28 Thiosulphate, tetra- and pentathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	100		
	S4O6(-2a)	500		
	S5O6(-2a)	500		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1040	1050	1050
	S8(g)	583	577	567
	H2S(a)	4.12	9.16	16.7
	S2O3(-2a)	7.2E-05	2.8E-04	7.8E-04
	HS(-a)	2.4E-05	1.5E-04	5.1E-04
	HSO3(-a)	2.3E-07	2.5E-06	2.1E-05
	H2SO3(a)	2.3E-08	4.6E-07	6.8E-06
	S4O6(-2a)	1.3E-08	1.2E-07	1.1E-06
	SO3(-2a)	5.2E-12	4.9E-11	3.0E-10
	S5O6(-2a)	2.8E-23	9.4E-22	2.5E-20
	S2O6(-2a)	1.9E-24	2.5E-22	2.3E-20
	S3O6(-2a)	2.0E-25	2.1E-23	1.5E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.29 Thiosulphate, tetra- and pentathionate 500 ppm, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	500		
	S4O6(-2a)	500		
	S5O6(-2a)	500		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1140	1140	1140
	S8(g)	524	524	523
	H2S(a)	0.388	0.881	1.65
	H2SO3(a)	2.4E-06	4.7E-05	6.7E-04
	S4O6(-2a)	1.6E-06	1.4E-05	1.2E-04
	S2O3(-2a)	7.5E-06	2.9E-05	8.4E-05
	HSO3(-a)	7.7E-07	8.3E-06	7.0E-05
	HS(-a)	7.1E-08	4.5E-07	1.7E-06
	SO3(-2a)	5.4E-13	5.2E-12	3.3E-11
	S5O6(-2a)	3.2E-21	1.0E-19	2.6E-18
	S2O6(-2a)	2.2E-22	2.9E-20	2.4E-18
	S3O6(-2a)	2.3E-23	2.4E-21	1.6E-19
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.30 Thiosulphate, tetra- and pentathionate 500 ppm, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	100		
	S3O6(-2a)	500		
	S4O6(-2a)	500		
	S5O6(-2a)	500		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1140	1150	1150
	S8(g)	522	519	513
	H2S(a)	2.12	4.8	8.93
	S2O3(-2a)	4.1E-05	1.6E-04	4.6E-04
	HS(-a)	5.0E-06	3.1E-05	1.1E-04
	HSO3(-a)	3.3E-07	3.6E-06	3.0E-05
	H2SO3(a)	8.2E-08	1.6E-06	2.3E-05
	S4O6(-2a)	5.2E-08	4.6E-07	4.1E-06
	SO3(-2a)	3.0E-12	2.9E-11	1.8E-10
	S5O6(-2a)	1.1E-22	3.5E-21	8.8E-20
	S2O6(-2a)	7.4E-24	9.7E-22	8.3E-20
	S3O6(-2a)	7.7E-25	8.0E-23	5.6E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.31 Thiosalt 500 ppm each, pH 1

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	500		
	S4O6(-2a)	500		
	S5O6(-2a)	500		
pH		1		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1370	1370	1370
	S8(g)	677	676	675
	H2S(a)	0.386	0.877	1.65
	H2SO3(a)	2.7E-06	5.3E-05	7.4E-04
	S4O6(-2a)	2.2E-06	1.9E-05	1.7E-04
	S2O3(-2a)	8.9E-06	3.5E-05	1.0E-04
	HSO3(-a)	8.7E-07	9.4E-06	7.9E-05
	HS(-a)	7.2E-08	4.6E-07	1.7E-06
	SO3(-2a)	6.3E-13	6.1E-12	3.8E-11
	S5O6(-2a)	4.6E-21	1.5E-19	3.8E-18
	S2O6(-2a)	2.9E-22	3.8E-20	3.2E-18
	S3O6(-2a)	3.2E-23	3.3E-21	2.2E-19
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.32 Thiosalt 500 ppm each, pH 8

Initial thiosalt concentration (ppm)	S2O3(-2a)	500		
	S3O6(-2a)	500		
	S4O6(-2a)	500		
	S5O6(-2a)	500		
pH		8		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	1370	1380	1380
	S8(g)	674	670	664
	H2S(a)	2.59	5.83	10.8
	S2O3(-2a)	6.0E-05	2.3E-04	6.6E-04
	HS(-a)	8.4E-06	5.3E-05	1.9E-04
	HSO3(-a)	3.4E-07	3.6E-06	3.1E-05
	H2SO3(a)	6.1E-08	1.2E-06	1.7E-05
	S4O6(-2a)	4.9E-08	4.4E-07	3.9E-06
	SO3(-2a)	4.2E-12	4.0E-11	2.5E-10
	S5O6(-2a)	1.0E-22	3.4E-21	8.7E-20
	S2O6(-2a)	6.5E-24	8.6E-22	7.4E-20
	S3O6(-2a)	7.1E-25	7.4E-23	5.2E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

Table A.33 Thiosalt 300 ppm each, pH 4.5

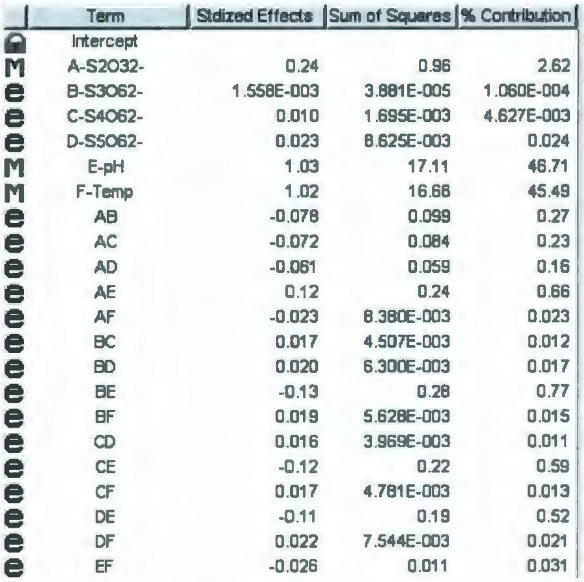
Initial thiosalt concentration (ppm)	S2O3(-2a)	300		
	S3O6(-2a)	300		
	S4O6(-2a)	300		
	S5O6(-2a)	300		
pH		4.5		
Temperature		-5	17.5	40
Decomposition products (ppm)	SO4(-2a)	827	831	838
	S8(g)	401	395	386
	H2S(a)	3.91	8.71	15.9
	S2O3(-2a)	5.4E-05	2.1E-04	5.9E-04
	HS(-a)	2.1E-05	1.3E-04	4.4E-04
	HSO3(-a)	2.0E-07	2.2E-06	1.9E-05
	H2SO3(a)	2.2E-08	4.4E-07	6.6E-06
	S4O6(-2a)	9.4E-09	8.6E-08	7.9E-07
	SO3(-2a)	4.1E-12	3.9E-11	2.4E-10
	S2O6(-2a)	1.4E-24	1.9E-22	1.7E-20
	S5O6(-2a)	1.9E-23	6.2E-22	1.7E-20
	S3O6(-2a)	1.4E-25	1.6E-23	1.1E-21
	HSO5(-a)	1.1E-31	1.1E-31	1.1E-31

APPENDIX B

Results from Design-Expert

Determination of significant factors effecting thiosulphate formation

Table B.1 Significant factors and % contribution to thiosulphate formation



	Term	Stdized Effects	Sum of Squares	% Contribution
🔒	Intercept			
M	A-S2032-	0.24	0.96	2.62
e	B-S3062-	1.558E-003	3.881E-005	1.060E-004
e	C-S4062-	0.010	1.695E-003	4.627E-003
e	D-S5062-	0.023	8.625E-003	0.024
M	E-pH	1.03	17.11	46.71
M	F-Temp	1.02	16.66	45.49
e	AB	-0.078	0.099	0.27
e	AC	-0.072	0.084	0.23
e	AD	-0.061	0.059	0.16
e	AE	0.12	0.24	0.66
e	AF	-0.023	8.380E-003	0.023
e	BC	0.017	4.507E-003	0.012
e	BD	0.020	6.300E-003	0.017
e	BE	-0.13	0.28	0.77
e	BF	0.019	5.628E-003	0.015
e	CD	0.016	3.969E-003	0.011
e	CE	-0.12	0.22	0.59
e	CF	0.017	4.781E-003	0.013
e	DE	-0.11	0.19	0.52
e	DF	0.022	7.544E-003	0.021
e	EF	-0.026	0.011	0.031

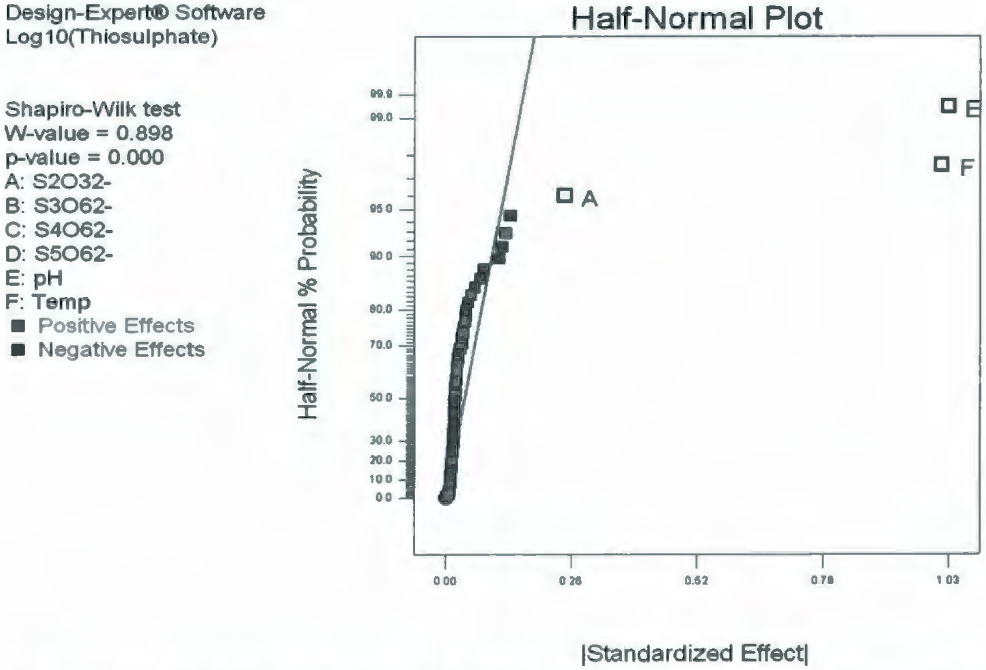
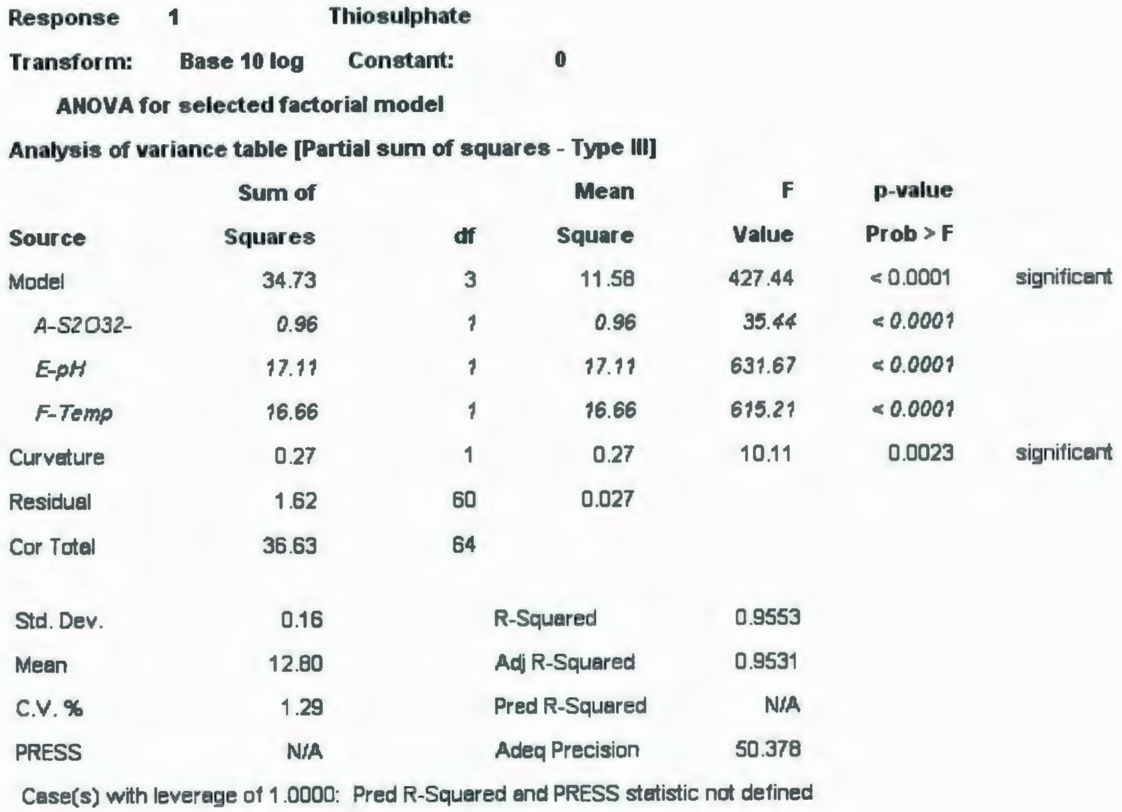


Figure B.1 Half-Normal Plot of factors effecting thiosulphate formation

Table B.2 Statistic of significant factors



Response **1** **Thiosulphate**

Transform: **Base 10 log** **Constant:** **0**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	34.73	3	11.58	427.44	< 0.0001	significant
A-S2O32-	*0.96*	*1*	*0.96*	*35.44*	*< 0.0001*	
E-pH	*17.11*	*1*	*17.11*	*631.67*	*< 0.0001*	
F-Temp	*16.66*	*1*	*16.66*	*615.21*	*< 0.0001*	
Curvature	0.27	1	0.27	10.11	0.0023	significant
Residual	1.62	60	0.027			
Cor Total	36.63	64				

Std. Dev.	0.16	R-Squared	0.9553
Mean	12.80	Adj R-Squared	0.9531
C.V. %	1.29	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	50.378

Case(s) with leverage of 1.0000: Pred R-Squared and PRESS statistic not defined

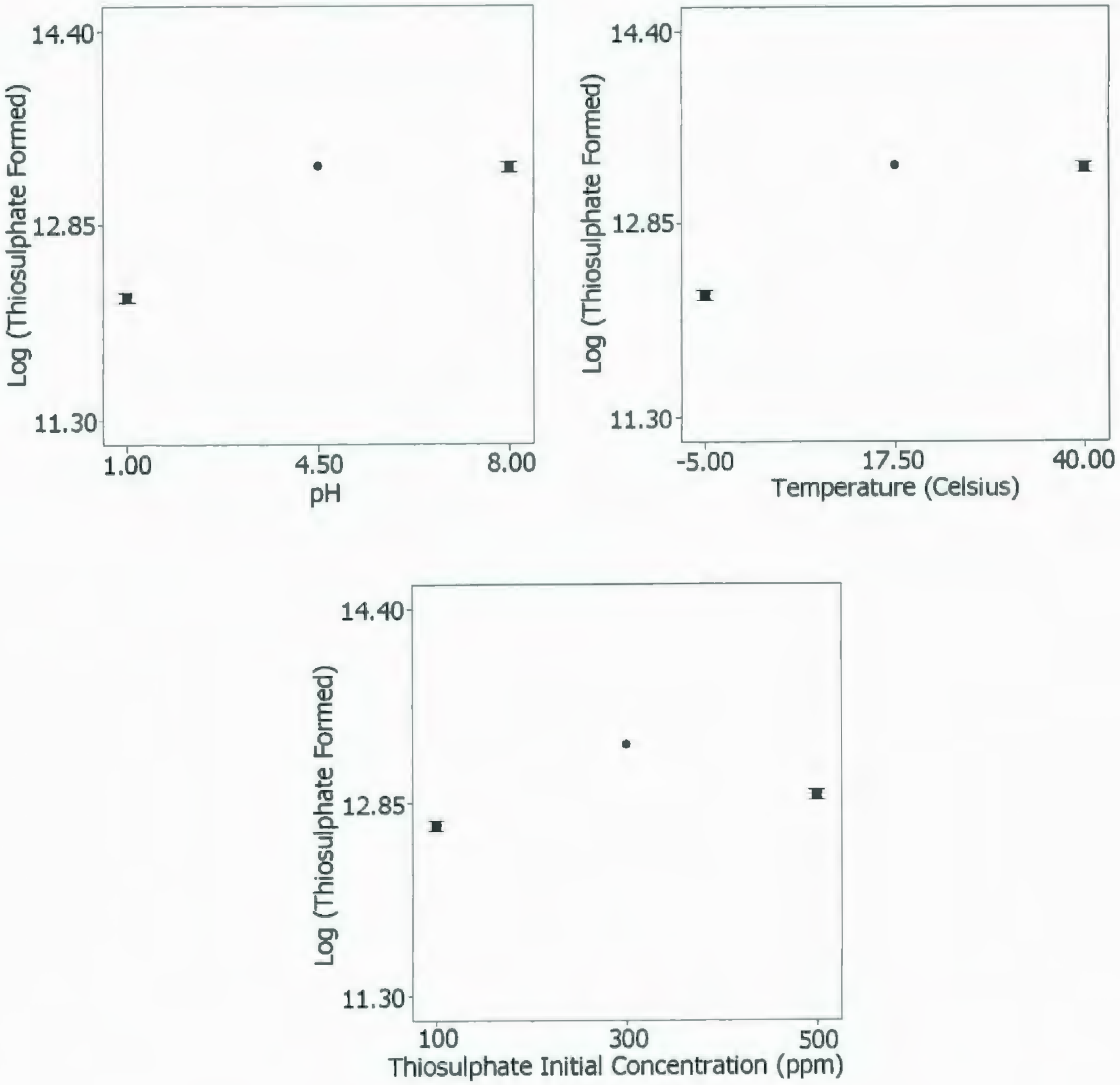
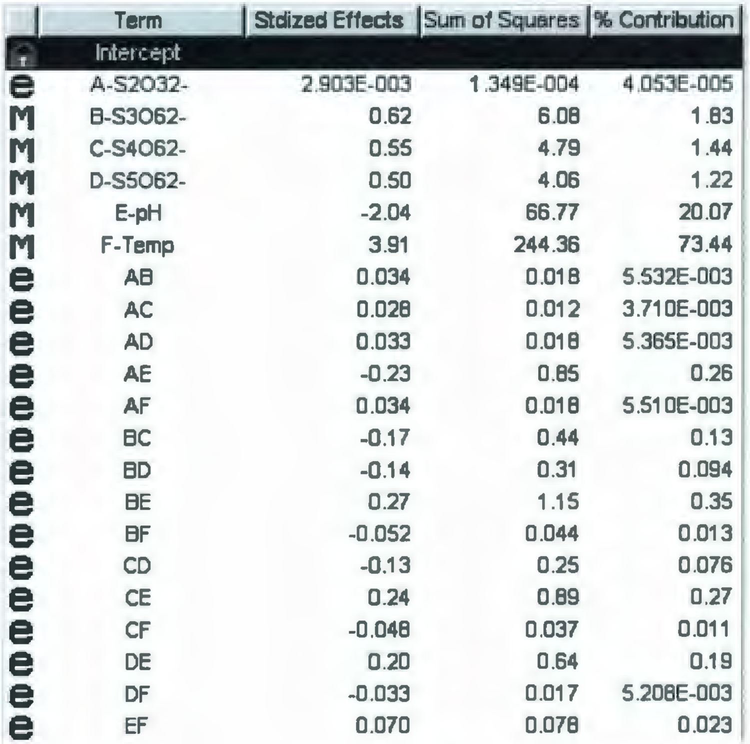


Figure B.2 Significant factors affecting thiosulphate formation

Determination of significant factors effecting trithionate formation

Table B.3 Significant factors and % contribution to trithionate formation



	Term	Stdized Effects	Sum of Squares	% Contribution
	Intercept			
e	A-S2O32-	2.903E-003	1.349E-004	4.053E-005
M	B-S3O62-	0.62	6.08	1.83
M	C-S4O62-	0.55	4.79	1.44
M	D-S5O62-	0.50	4.06	1.22
M	E-pH	-2.04	66.77	20.07
M	F-Temp	3.91	244.36	73.44
e	AB	0.034	0.018	5.532E-003
e	AC	0.028	0.012	3.710E-003
e	AD	0.033	0.018	5.365E-003
e	AE	-0.23	0.85	0.26
e	AF	0.034	0.018	5.510E-003
e	BC	-0.17	0.44	0.13
e	BD	-0.14	0.31	0.094
e	BE	0.27	1.15	0.35
e	BF	-0.052	0.044	0.013
e	CD	-0.13	0.25	0.076
e	CE	0.24	0.89	0.27
e	CF	-0.048	0.037	0.011
e	DE	0.20	0.64	0.19
e	DF	-0.033	0.017	5.208E-003
e	EF	0.070	0.078	0.023

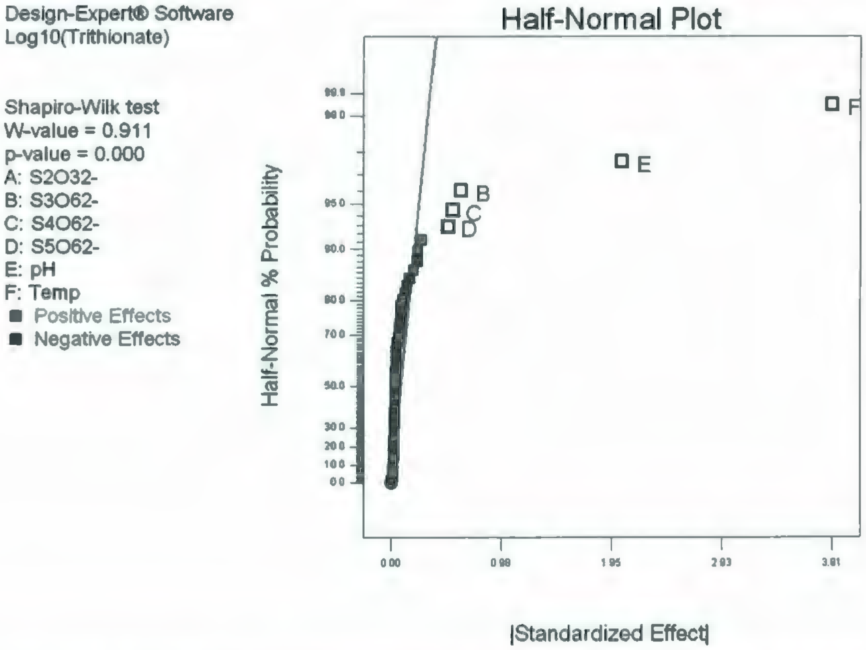


Figure B.3 Half-Normal Plot of factors effecting trithionate formation

Table B.4 Statistic of significant factors

Response	**2**	**Trithionate**		
Transform:	**Base 10 log**	**Constant:**	**0**	

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	326.06	5	65.21	613.29	< 0.0001	significant
B-S3O62-	*6.08*	*1*	*6.08*	*57.18*	*< 0.0001*	
C-S4O62-	*4.79*	*1*	*4.79*	*45.03*	*< 0.0001*	
D-S5O62-	*4.06*	*1*	*4.06*	*38.16*	*< 0.0001*	
E-pH	*66.77*	*1*	*66.77*	*627.95*	*< 0.0001*	
F-Temp	*244.36*	*1*	*244.36*	*2298.12*	*< 0.0001*	
Curvature	0.53	1	0.53	4.98	0.0296	significant
Residual	6.17	58	0.11			
Cor Total	332.75	64				

Std. Dev.	0.33	R-Squared	0.9814
Mean	-5.09	Adj R-Squared	0.9798
C.V. %	6.41	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	71.190

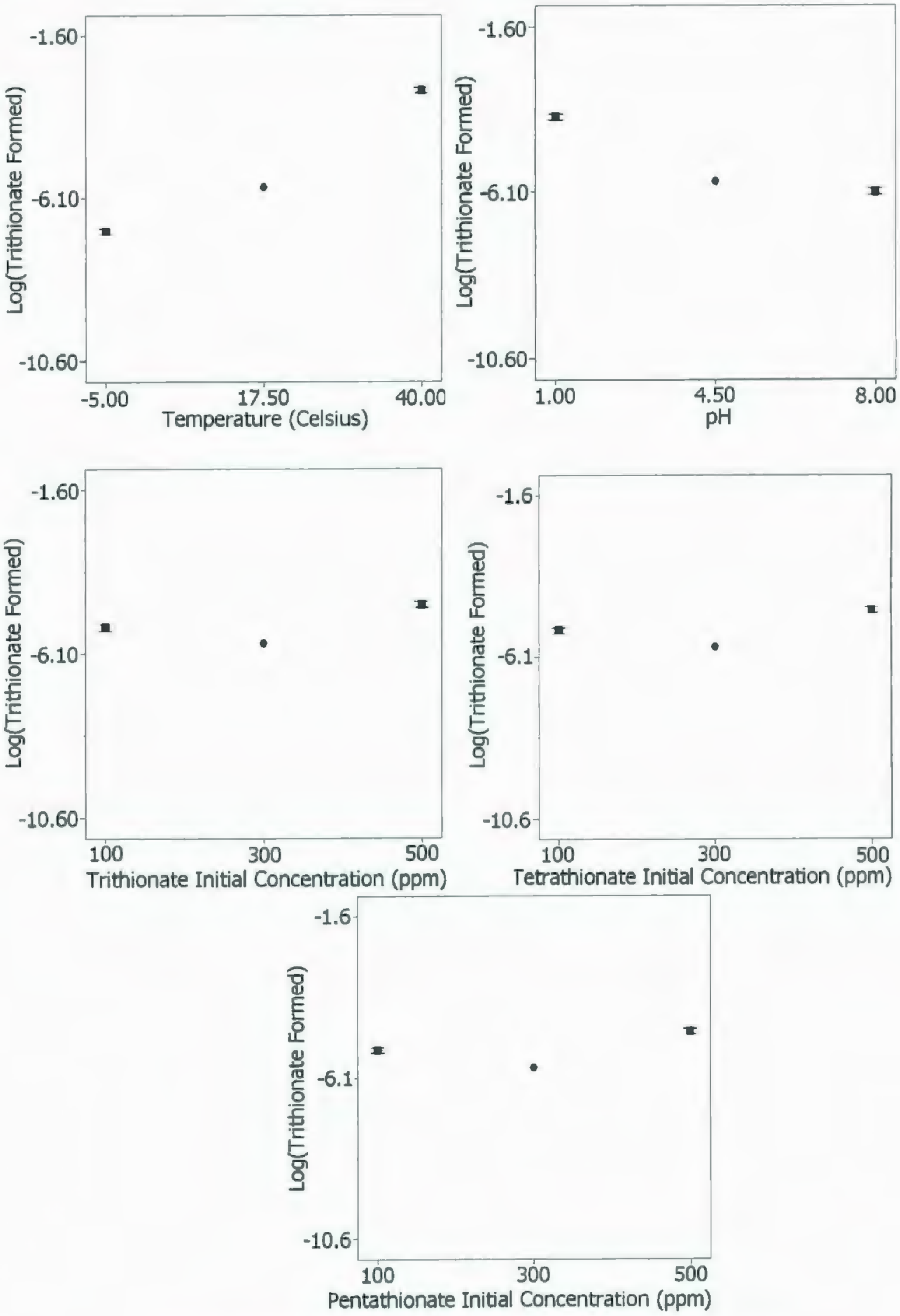
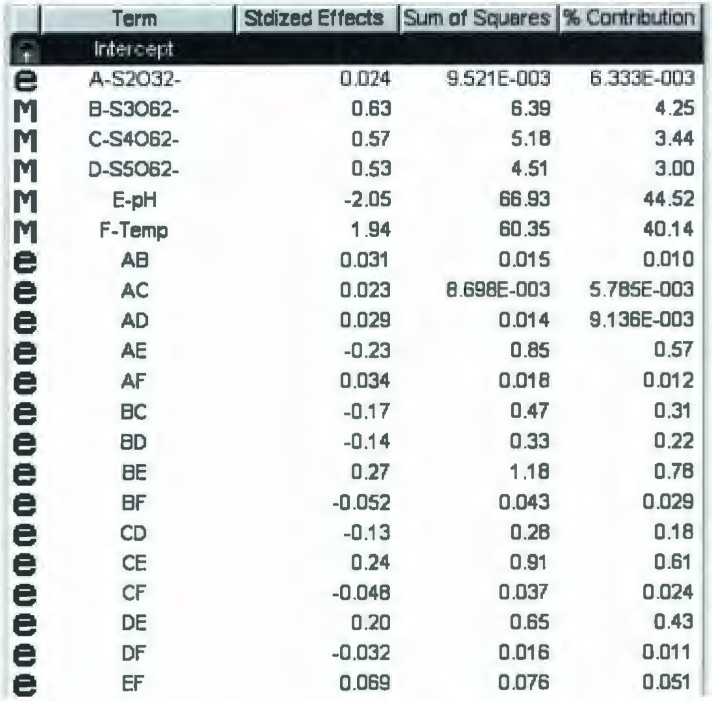


Figure B.4 Significant factors affecting trithionate formation

Determination of significant factors effecting tetrathionate formation

Table B.5 Significant factors and % contribution to tetrathionate formation



	Term	Stdized Effects	Sum of Squares	% Contribution
	Intercept			
e	A-S2O32-	0.024	9.521E-003	6.333E-003
M	B-S3O62-	0.63	6.39	4.25
M	C-S4O62-	0.57	5.18	3.44
M	D-S5O62-	0.53	4.51	3.00
M	E-pH	-2.05	66.93	44.52
M	F-Temp	1.94	60.35	40.14
e	AB	0.031	0.015	0.010
e	AC	0.023	8.698E-003	5.785E-003
e	AD	0.029	0.014	9.136E-003
e	AE	-0.23	0.85	0.57
e	AF	0.034	0.018	0.012
e	BC	-0.17	0.47	0.31
e	BD	-0.14	0.33	0.22
e	BE	0.27	1.18	0.78
e	BF	-0.052	0.043	0.029
e	CD	-0.13	0.28	0.18
e	CE	0.24	0.91	0.61
e	CF	-0.048	0.037	0.024
e	DE	0.20	0.65	0.43
e	DF	-0.032	0.016	0.011
e	EF	0.069	0.076	0.051

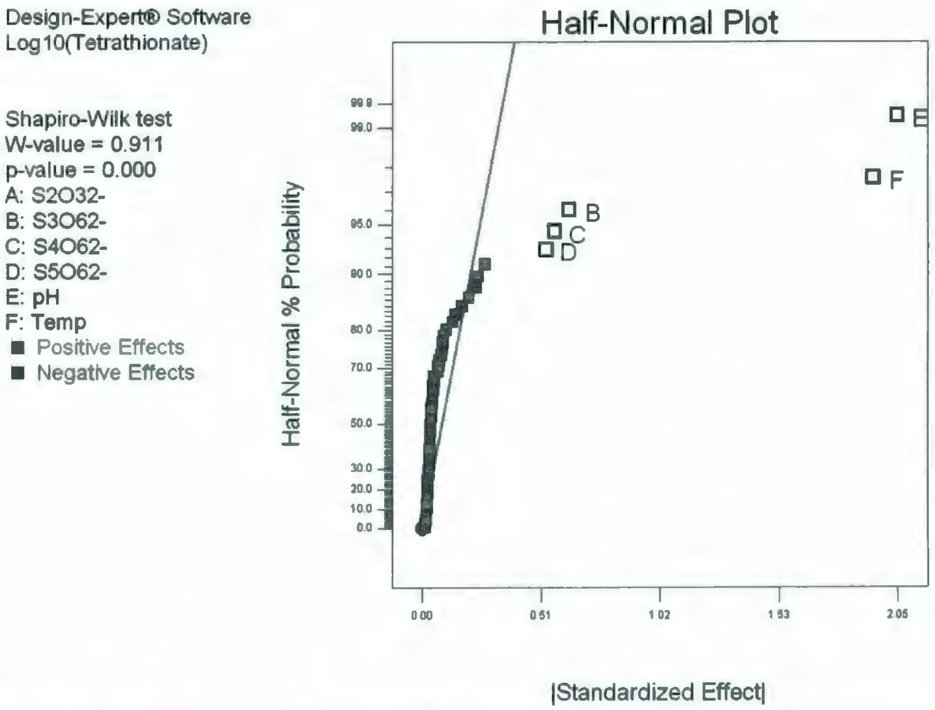
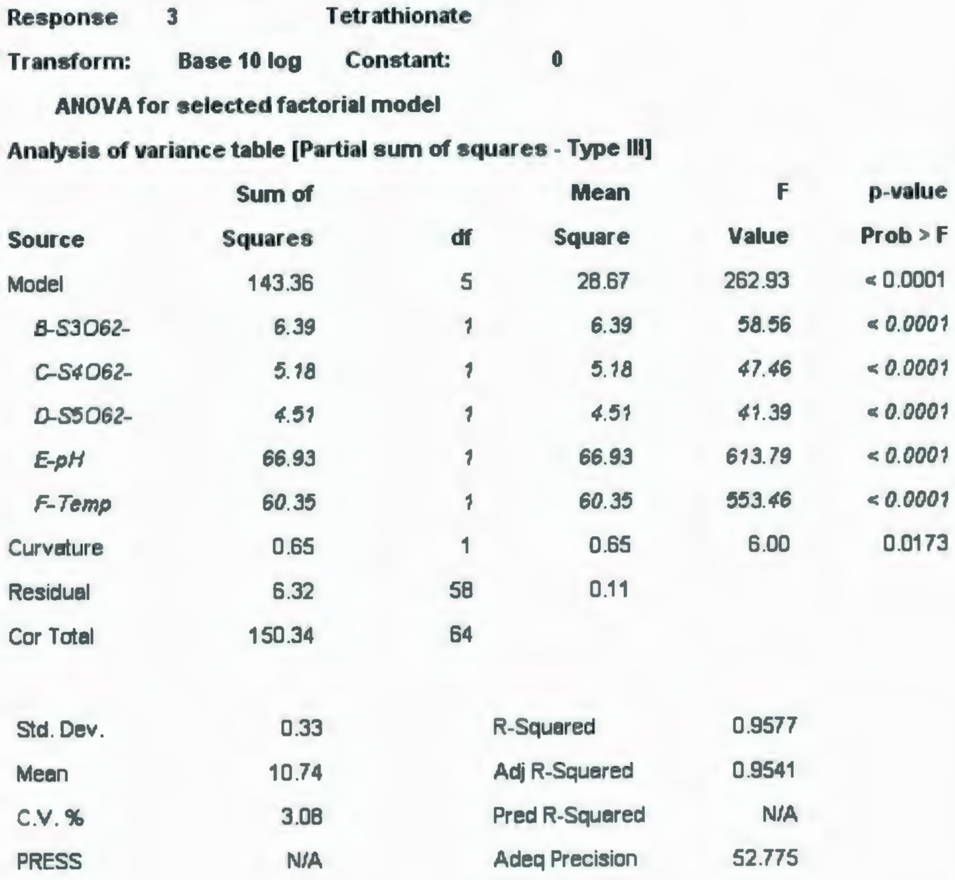


Figure B.5 Half-Normal Plot of factors effecting tetrathionate formation

Table B.6 Statistic of significant factors



Response **3** **Tetrathionate**

Transform: **Base 10 log** **Constant:** **0**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	143.36	5	28.67	262.93	< 0.0001
B-S3O62-	*6.39*	*1*	*6.39*	*58.56*	*< 0.0001*
C-S4O62-	*5.18*	*1*	*5.18*	*47.46*	*< 0.0001*
D-S5O62-	*4.51*	*1*	*4.51*	*41.39*	*< 0.0001*
E-pH	*66.93*	*1*	*66.93*	*613.79*	*< 0.0001*
F-Temp	*60.35*	*1*	*60.35*	*553.46*	*< 0.0001*
Curvature	0.65	1	0.65	6.00	0.0173
Residual	6.32	58	0.11		
Cor Total	150.34	64			

Std. Dev.	0.33	R-Squared	0.9577
Mean	10.74	Adj R-Squared	0.9541
C.V. %	3.08	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	52.775

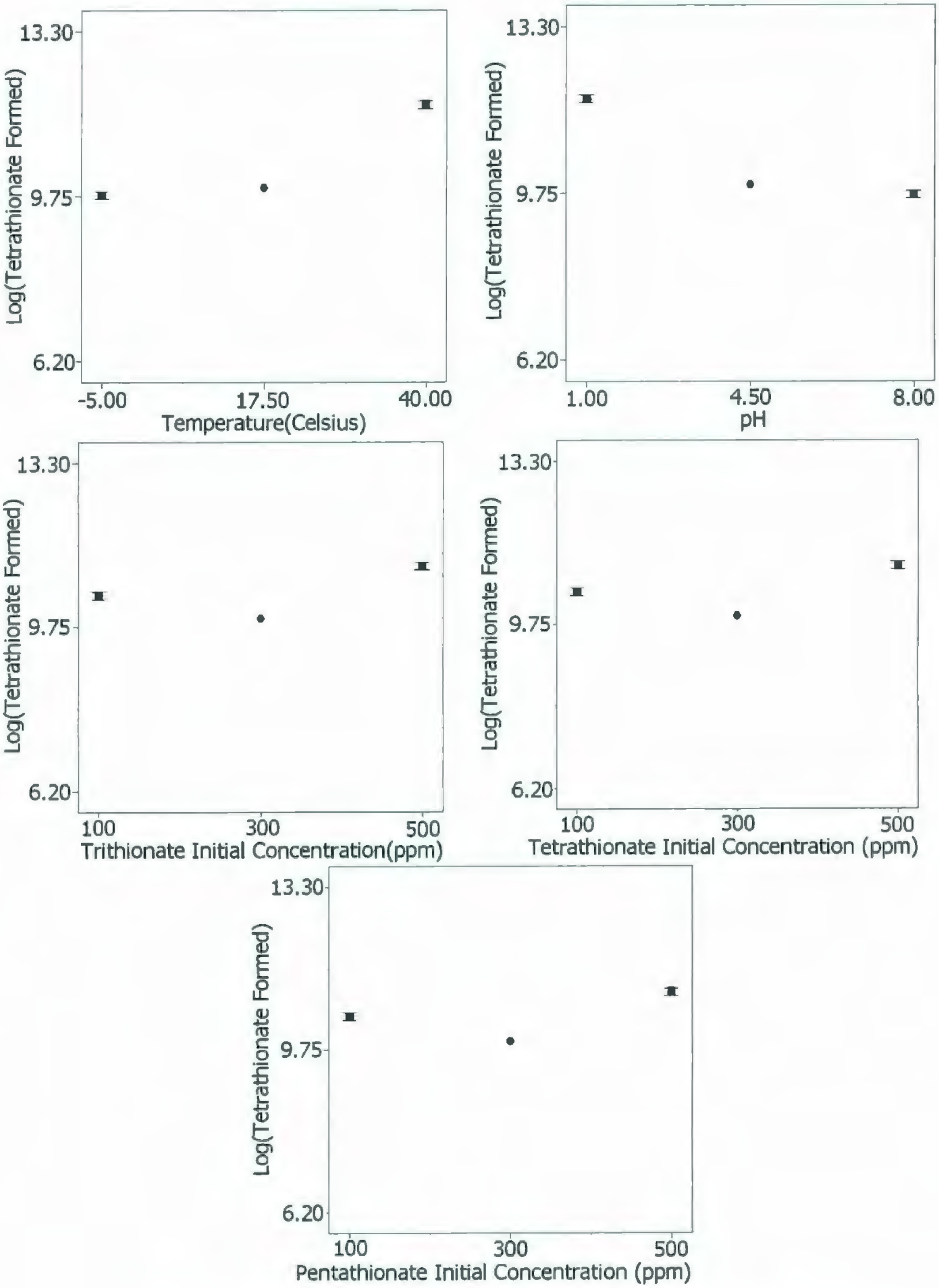
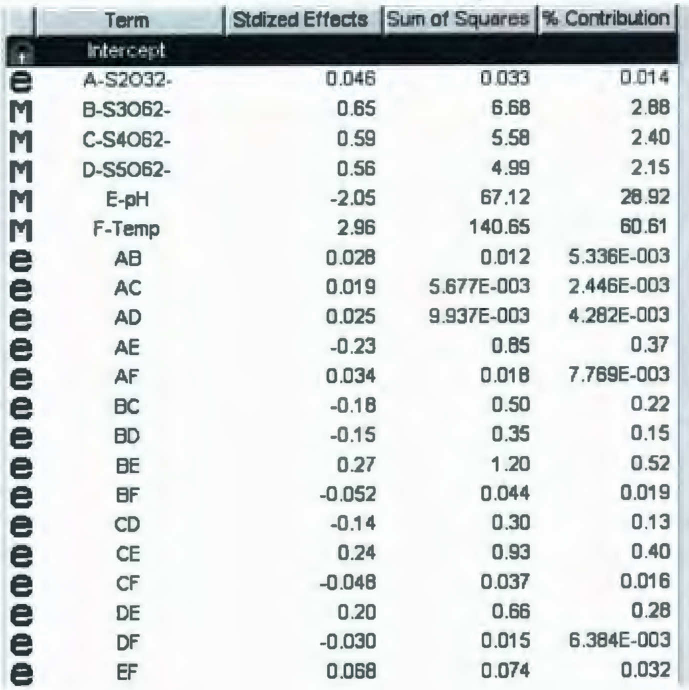


Figure B.6 Significant factors affecting tetrathionate formation

Determination of significant factors effecting pentathionate formation

Table B.7 Significant factors and % contribution to pentathionatethionate formation



	Term	Stdized Effects	Sum of Squares	% Contribution
	Intercept			
e	A-S2O32-	0.046	0.033	0.014
M	B-S3O62-	0.65	6.68	2.88
M	C-S4O62-	0.59	5.58	2.40
M	D-S5O62-	0.56	4.99	2.15
M	E-pH	-2.05	67.12	28.92
M	F-Temp	2.96	140.65	60.61
e	AB	0.028	0.012	5.336E-003
e	AC	0.019	5.677E-003	2.446E-003
e	AD	0.025	9.937E-003	4.282E-003
e	AE	-0.23	0.85	0.37
e	AF	0.034	0.018	7.769E-003
e	BC	-0.18	0.50	0.22
e	BD	-0.15	0.35	0.15
e	BE	0.27	1.20	0.52
e	BF	-0.052	0.044	0.019
e	CD	-0.14	0.30	0.13
e	CE	0.24	0.93	0.40
e	CF	-0.048	0.037	0.016
e	DE	0.20	0.66	0.28
e	DF	-0.030	0.015	6.384E-003
e	EF	0.068	0.074	0.032

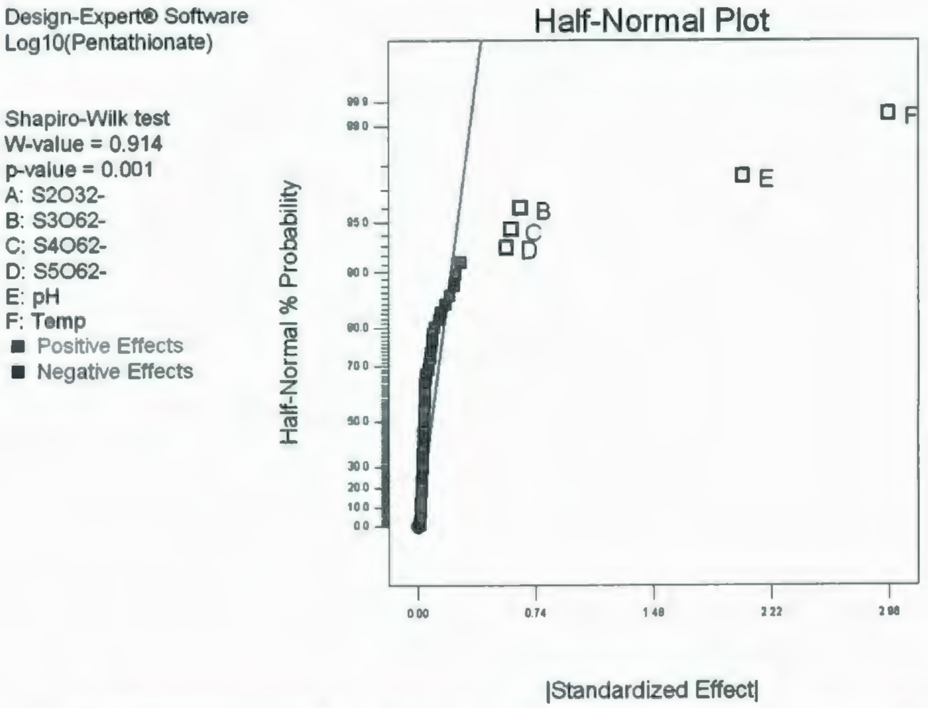
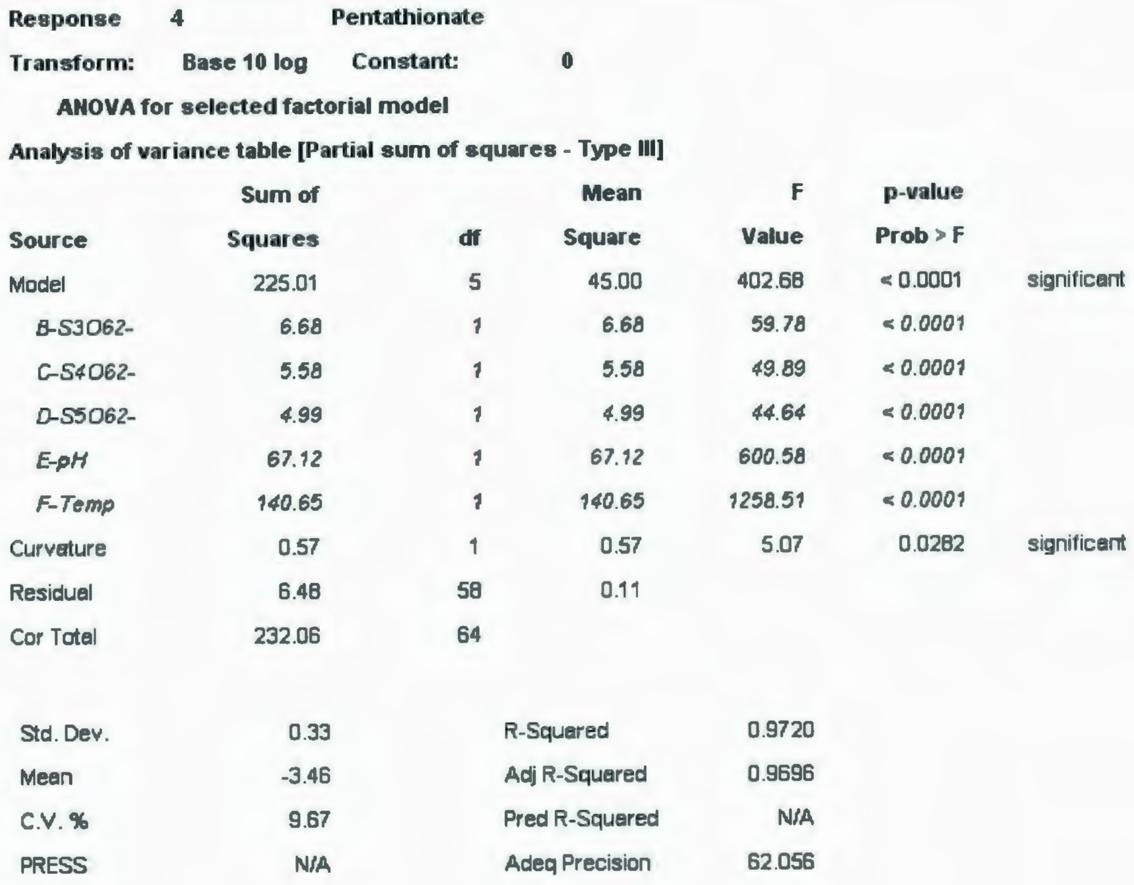


Figure B.7 Half-Normal Plot of factors effecting pentathionate formation

Table B.8 Statistic of significant factors



Response **4** **Pentathionate**

Transform: **Base 10 log** **Constant:** **0**

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	225.01	5	45.00	402.68	< 0.0001	significant
B-S3O62-	*6.68*	*1*	*6.68*	*59.78*	*< 0.0001*	
C-S4O62-	*5.58*	*1*	*5.58*	*49.89*	*< 0.0001*	
D-S5O62-	*4.99*	*1*	*4.99*	*44.64*	*< 0.0001*	
E-pH	*67.12*	*1*	*67.12*	*600.58*	*< 0.0001*	
F-Temp	*140.65*	*1*	*140.65*	*1258.51*	*< 0.0001*	
Curvature	0.57	1	0.57	5.07	0.0282	significant
Residual	6.48	58	0.11			
Cor Total	232.06	64				

Std. Dev.	0.33	R-Squared	0.9720
Mean	-3.46	Adj R-Squared	0.9696
C.V. %	9.67	Pred R-Squared	N/A
PRESS	N/A	Adeq Precision	62.056

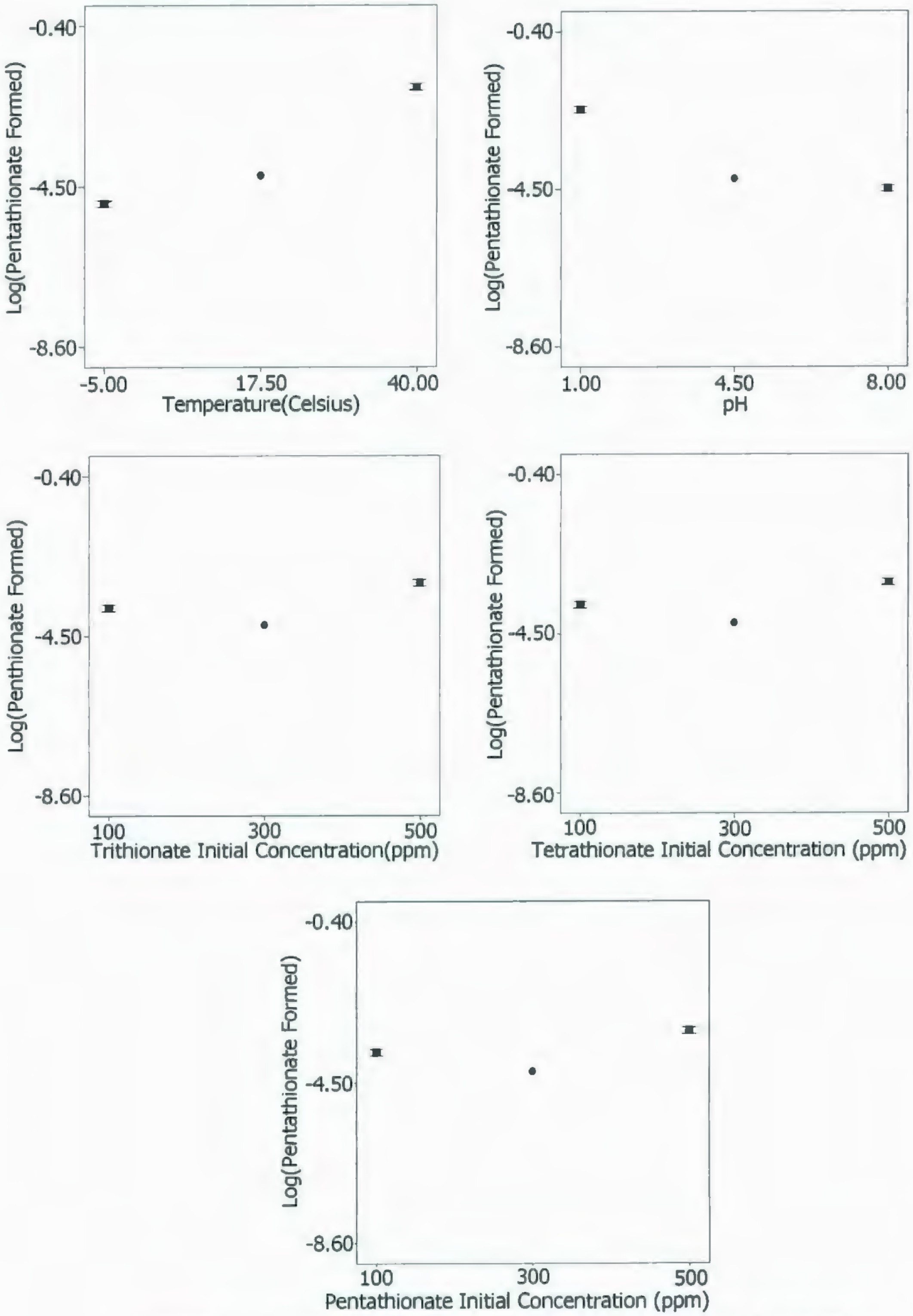


Figure B.8 Significant factors affecting pentathionate formation

APPENDIX C

Results from Thiosalt Kinetic Study

Each table shows pH values, and concentrations of thiosalt, sulphate, and dissolved oxygen as a function of time for each experiment

Thiosulphate Experiments

Table C.1 Thiosulphate 250 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	250	0	0	0	2.09
6	231	0	0		1.90
9	218	2	0		1.99
24	200	3	0	6	1.98
30	193	3	0		1.97
48	174	12	0	9	2.02
72	157	14	0	17	2.03

Table C.2 Thiosulphate 500 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	2	8	0	2.13
9	454	5	2		2.00
24	393	14	1	17	1.91
48	341	14	5	21	1.91
72	310	22	5	22	1.96

Table C.3 Thiosulphate 1000 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	1000	3	0	10	2.10
3	892	47	0		1.97
6	866	23	0		1.97
9	816	19	0	11	1.96
24	646	31	0	19	1.97
48	609	56	0	40	2.07
72	579	79	0	46	2.03

Table C.4 Thiosulphate 250 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	250	0	11	0	2.13
3	226	1	6		2.15
6	201	0	4		2.14
9	185	7	3	0	2.15
24	125	3	12	0	2.16
48	98	2	16	13	2.21
72	74	4	23	13	2.22

Table C.5 Thiosulphate 500 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	0	5	0	2.12
1	476	0	3		
3	422	8	4		2.17
6	356	2	4		2.17
9	327	8	1	0	2.19
24	213	10	16	15	2.22
48	163	18	28	22	2.25
72	141	21	35	23	2.28

Table C.6 Thiosulphate 1000 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	1000	0	4	0	2.11
1	861	1	3		
3	738	5	6		2.23
6	615	20	1		2.23
9	540	25	5	15	2.27
24	397	62	8	35	2.29
48	343	89	26	56	2.35
72	319	104	37	67	2.36

Table C.7 Thiosulphate 250 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	250	3	12	0	2.11
3	200	5	4		1.91
6	159	8	7		1.91
9	134	7	5		1.94
24	81	9	14	10	1.95
48	53	9	23	11	1.78
72	42	11	33	21	1.78

Table C.8 Thiosulphate 500 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	1	3	0	2.10
1	433	3	6		
3	307	7	3		1.98
6	248	15	1		1.96
9	210	18	1	8	2.00
24	127	33	8	20	2.01
48	100	35	23	25	1.87
72	91	36	35	33	1.88

Table C.9 Thiosulphate 1000 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	1000	1	5	0	2.11
1	752	7	2		
3	507	28	1		2.03
6	385	45	1		2.06
9	330	56	1	20	2.09
24	262	96	2	41	2.12
48	244	125	13	56	2.00
72	220	131	23	59	2.01

Table C.10 Thiosulphate 250 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	250	0	0	4.15
6	253	0	0	3.99
24	253	0	0	3.98
30	256	0	0	4.04
48	256	0	0	3.97
72	249	2	0	3.99

Table C.11 Thiosulphate 500 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	500	1	1	4.17
24	504	3	2	4.04
48	481	0	1	4.06
72	496	0	2	4.08

Table C.12 Thiosulphate 1000 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	1000	0	0	4.18
24	979	0	1	3.97
48	999	0	1	4.02
72	1002	0	0	4.00

Table C.13 Thiosulphate 250 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	250	0	0	3.96	8.19
6	243	0	0	3.99	8.14
24	243	0	0	4.00	8.22
48	242	5	0	3.98	8.31
72	239	0	1	3.96	8.01

Table C.14 Thiosulphate 500 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	500	0	3	3.99	8.62
24	500	2	3	4.05	8.68
48	497	1	4	4.13	8.76
72	497	0	3	4.09	8.24

Table C.15 Thiosulphate 1000 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	1000	0	0	0	4.00	8.48
24	989	2	0	11	3.99	8.91
48	991	3	1	20	4.01	9.08
72	989	3	2	25	4.01	9.17

Table C.16 Thiosulphate 250 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	250	0	0	3.94	8.30
24	250	0	1	3.86	8.22
48	248	2	1	3.85	8.04
72	247	5	1	3.83	8.67

Table C.17 Thiosulphate 500 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	0	6	0	4.10
24	505	5	3	0	4.00
48	502	2	3	0	4.00
72	477	7	11	0	4.00

Table C.18 Thiosulphate 1000 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	1000	5	1	3.97	8.15
6	1010	9	1	3.87	8.30
24	981	8	2	3.88	8.13
30	1019	0	1	3.86	8.16
48	1009	2	1	3.86	8.02
72	992	3	2	3.86	7.91

Table C.19 Thiosulphate 250 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	250	0	1	6.91
24	251	3	0	6.81
48	258	3	0	6.92
72	253	0	0	6.93

Table C.20 Thiosulphate 500 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	500	0	2	6.93
24	496	0	1	6.85
48	504	0	1	6.89
72	500	0	2	6.93

Table C.21 Thiosulphate 1000 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	1000	0	0	7.01
24	983	2	1	6.84
48	1000	0	1	6.79
72	1033	0	0	6.89

Table C.22 Thiosulphate 250 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	250	0	0	6.96	8.21
6	247	0	0	6.97	8.35
30	244	0	0	6.96	8.24
48	251	1	2	6.94	8.35
72	273	0	1	6.92	8.46

Table C.23 Thiosulphate 500 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	500	0	1	6.95	8.13
30	512	0	2	6.94	8.32
48	507	11	1	6.93	8.43
72	497	0	3	6.90	8.41

Table C.24 Thiosulphate 1000 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	1000	2	0	6.99	8.66
24	1017	0	1	6.96	9.30
48	1011	3	2	6.94	9.21
72	1013	2	4	6.93	9.48

Table C.25 Thiosulphate 250 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	250	0	0	6.95	8.23
6	255	0	3	6.92	8.30
24	242	0	3	6.88	8.26
30	248	0	5	6.90	7.87
48	246	0	8	6.96	7.60
72	242	0	13	6.97	7.72

Table C.26 Thiosulphate 500 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	500	0	0	6.97	8.21
24	525	0	2	6.94	7.62
48	501	0	4	6.96	7.33
72	506	2	7	7.03	7.67

Table C.27 Thiosulphate 1000 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	1000	0	0	6.96	8.34
6	1002	0	3	6.92	8.46
24	981	12	5	6.90	8.08
30	981	10	3	6.90	7.75
48	994	0	5	6.91	7 84
72	1023	3	9	6.95	7.59

Table C.28 Thiosulphate 250 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	250	9	21	8.96
30	268	3	11	8.94
72	254	7	22	8.89

Table C.29 Thiosulphate 500 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	2	17	0	8.99
6	509	0	7		9.16
30	495	2	12	0	8.94
48	503	2	10	0	8.90
72	474	8	31	0	8.92

Table C.30 Thiosulphate 1000 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	1000	6	13	9.05
30	1007	0	7	9.09
72	995	6	22	9.06

Table C.31 Thiosulphate 250 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	250	2	6	8.75	8.19
3.5	251	1	5	8.75	8.27
7	251	0	5	8.73	8.25
24	259	5	0	8.74	8.22
48	259	10	13	8.70	8.12
72	256	15	13	8.69	8.20

Table C.32 Thiosulphate 500 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	3	16	0	8.90
24	480	8	23	0	8.98
48	495	8	9	0	8.97
72	479	14	13	0	8.93

Table C.33 Thiosulphate 1000 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	1000	5	20	0	8.92
24	993	7	22	0	9.03
48	1007	14	13	0	9.01
72	983	17	20	0	8.99

Table C.34 Thiosulphate 250 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	250	5	12	0	8.99
6	249	8	11		8.87
24	192	42	11	18	8.83
48	160	79	5	43	8.80
72	104	121	7	69	8.79
96	82	137	4	106	8.80

Table C.35 Thiosulphate 500 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	5	19	0	9.01
6	483	11	27		8.89
24	456	29	24	6	8.79
48	436	48	21	12	8.60
72	429	66	13	16	8.57
96	429	86	7	26	8.58

Table C.36 Thiosulphate 1000 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	1000	3	17	0	9.02
6	987	8	23		8.88
24	960	15	14	4	8.85
48	960	29	20	4	8.83
72	927	39	24	6	8.82
96	927	45	27	8	8.83

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Table C.37 Trithionate 250 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	250	0	2.14
24	0	254	0	1.92
30	2	248	0	1.97
48	2	249	0	1.95
72	3	248	0	1.94

Table C.38 Trithionate 500 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	500	0	2.15
6	0	506	0	2.07
48	0	504	0	2.11
72	3	502	0	2.14

Table C.39 Trithionate 1000 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	1000	0	0	2.11
24	1	997	1	0	1.89
30	1	999	1		1.93
48	2	995	1	11	1.91
72	4	989	0	12	1.94

Table C.40 Trithionate 250 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	250	0	1.99	8.21
6	0	248	1	2.02	8.21
24	2	245	0	2.00	8.24
30	2	249	1	2.04	8.20
48	3	243	0	2.04	8.32
72	4	245	1	2.04	8.03

Table C.41 Trithionate 500 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	500	1	0	1.85	8.81
24	0	501	1	8	1.95	8.69
30	4	502	2		1.92	8.57
48	3	472	4	10	1.99	9.20
72	4	480	4	18	2.01	8.72

Table C.42 Trithionate 1000 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	1000	0	0	1.92	8.57
24	6	990	1	11	1.95	8.64
48	11	986	3	13	1.97	8.65
72	8	965	15	21	2.04	9.00

Table C.43 Trithionate 250 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	250	1	0	1.90	8.14
6	0	247	1		1.85	7.52
24	8	244	1	10	1.79	8.66
48	11	233	2	19	1.83	8.74
72	12	209	1	23	1.77	8.93

Table C.44 Trithionate 500 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	500	1	0	1.90	8.60
6	4	490	0		1.90	8.62
24	13	468	1	11	1.91	8.57
48	17	435	3	26	1.90	9.10
72	19	419	4	36	1.95	9.01

Table C.45 Trithionate 1000 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	1000	0	10	1.92	8.41
6	8	930	2	16	1.83	8.85
24	22	917	5	35	1.83	8.35
48	35	864	10	57	1.85	8.08
72	40	806	10	72	1.85	7.76

Table C.46 Trithionate 250 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	250	0	0	4.18
24	0	250	0	0	3.99
30	0	246	0		4.02
48	3	244	0	0	3.96
72	2	244	0	0	3.98

Table C.47 Trithionate 500 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	500	0	14	4.15
24	0	491	0	11	4.05
48	2	496	0	8	4.09
72	3	490	0	12	4.06

Table C.48 Trithionate 1000 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	1000	0	0	4.17
24	2	1010	1	10	3.99
30	3	1009	1		4.00
48	4	970	0	13	3.93
72	6	991	0	22	3.97

Table C.49 Trithionate 250 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	250	0	0	3.95	8.21
6	0	243	0		3.98	8.25
24	3	236	0	0	3.98	8.26
30	3	232	0		3.98	8.20
48	5	239	0	0	3.96	8.38
72	6	229	1	15	3.96	8.20

Table C.50 Trithionate 500 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	500	6	0	3.99	8.79
24	4	500	7	0	4.05	8.46
30	5	491	8		4.06	8.39
48	8	495	3	6	4.12	8.46
72	13	485	3	15	4.10	8.30

Table C.51 Trithionate 1000 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	1000	0	0	3.99	8.66
24	10	998	0	14	3.98	8.82
48	19	983	1	17	3.97	8.91
72	29	955	2	21	4.00	8.98

Table C.52 Trithionate 250 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	250	0	0	3.94	8.13
6	3	245	1		3.91	7.06
24	13	222	1	13	3.88	8.43
48	23	203	0	24	3.85	8.36
72	36	189	1	37	3.80	8.63

Table C.53 Trithionate 500 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	500	1	0	3.95	8.07
6	7	481	2		3.82	8.93
24	24	453	1	27	3.83	9.12
30	29	436	1		4.01	8.84
48	45	406	2	48	3.88	8.98
72	67	379	4	74	3.81	10.02

Table C.54 Trithionate 1000 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	1000	0	0	3.96	8.48
6	13	977	0	18	3.89	8.72
24	58	903	2	53	3.89	8.26
48	101	806	4	99	3.86	8.18
72	149	752	7	135	3.86	7.76

Table C.55 Trithionate 250 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	250	0	6.99
24	0	248	0	6.90
48	0	248	0	6.87
72	0	243	0	6.93

Table C.56 Trithionate 500 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	500	0	6.91
24	0	500	0	6.82
48	1	500	0	6.92
72	3	494	0	6.95

Table C.57 Trithionate 1000 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	1000	0	0	7.04
24	2	975	1	0	6.90
30	3	993	1		6.92
48	4	1004	2	0	6.88
72	7	990	1	0	6.91

Table C.58 Trithionate 250 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	250	0	0	6.97	8.30
6	0	250	0		6.98	8.33
24	3	242	0	0	6.95	8.35
30	4	241	0		6.96	8.23
48	5	242	0	0	6.95	8.28
72	8	231	0	0	6.95	8.17

Table C.59 Trithionate 500 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	500	0	0	6.95	8.11
6	0	494	0		6.96	8.12
24	5	504	1	0	6.95	8.22
48	10	483	1	0	6.96	8.17
72	14	471	2	14	6.96	8.20

Table C.60 Trithionate 1000 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	1000	0	0	7.00	8.69
6	4	997	2		6.98	8.99
24	10	950	1	14	6.95	9.05
48	20	943	1	31	6.86	9.19
72	31	924	2	24	6.83	9.30

Table C.61 Trithionate 250 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	250	0	0	6.98	8.06
6	4	245	0		6.94	8.02
24	15	237	0	10	6.94	7.73
30	19	222	1		6.93	7.30
48	43	207	1	26	6.94	7.74
72	38	188	2	35	6.94	7.46

Table C.62 Trithionate 500 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	500	0	0	6.98	8.19
6	8	491	1		6.97	7.24
24	31	481	2	28	6.93	8.06
30	39	476	2		6.93	7.97
48	56	410	3	50	6.93	7.55
72	79	371	6	71	6.88	8.62

Table C.63 Trithionate 1000 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	3	1000	0	0	6.92	8.30
6	19	965	1	9	6.87	7.58
24	59	898	3	53	6.84	7.82
30	74	886	3		6.83	7.84
48	112	825	7	101	6.85	7.61
72	147	743	16	142	6.89	7.40

Table C.64 Trithionate 250 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	250	0	8.93
24	0	254	0	8.96
48	2	254	0	8.92
72	2	257	0	8.95

Table C.65 Trithionate 500 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	500	0	0	9.04
24	0	501	0	0	9.08
48	0	491	0	0	8.95
72	0	482	0	0	9.02

Table C.66 Trithionate 1000 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	1	1000	1	0	9.08
6	2	995	0		9.26
25	1	990	0	0	9.37
30	1	988	0		9.44
48	3	966	0	12	9.43
72	4	964	0	18	9.35

Table C.67 Trithionate 250 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	250	0	8.73	8.14
3.5	0	248	0	8.75	8.26
7	0	248	0	8.73	8.36
24	0	259	0	8.74	8.20
30	5	256	0	8.72	8.13
48	7	256	0	8.71	8.08
72	8	251	0	8.72	8.10

Table C.68 Trithionate 500 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	500	0	8.73	7.94
3.5	0	508	0	8.75	8.13
7	0	507	0	8.76	8.23
24	5	528	0	8.76	8.38
48	11	510	0	8.74	8.30
72	15	506	0	8.74	8.43

Table C.69 Trithionate 1000 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	2	1000	0	0	8.90
24	11	986	0	16	9.04
48	21	937	4	21	9.00
72	30	953	2	32	8.97

Table C.70 Trithionate 250 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	250	0	0	8.83	9.02
7	4	243	1		8.70	8.15
24	13	238	5	12	8.66	8.40
48	20	234	2	29	8.57	8.08
72	16	216	4	42	8.55	7.86

Table C.71 Trithionate 500 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	500	0	0	8.83	8.99
7	6	490	2		8.71	8.40
24	23	494	6	0	8.70	8.44
30	27	486	7		8.64	8.26
48	30	472	7	55	8.59	8.00
72	34	442	6	88	8.54	8.18

Table C.72 Trithionate 1000 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	14	1000	5	0	8.82	8.73
7	17	984	1	23	8.74	7.98
24	45	962	3	58	8.66	8.24
48	76	926	3	108	8.56	7.96
72	103	858	8	168	8.49	7.91

Tetrathionate Experiments

Table C.73 Tetrathionate 250 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	3	250	2.15
24	0	3	259	1.96
30	0	2	251	1.95
48	0	3	247	1.93
72	0	3	252	1.94

Table C.74 Tetrathionate 500 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	0	500	0	2.23
24	0	2	501	0	2.09
48	0	0	503	0	2.12
72	0	8	488	0	2.17

Table C.75 Tetrathionate 1000 ppm, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	6	1000	2.15
24	0	3	1039	1.97
30	0	2	995	1.99
48	0	2	985	1.97
72	0	1	997	2.00

Table C.76 Tetrathionate 250 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	0	250	1.95	8.29
6	0	0	250	2.00	8.13
24	0	0	256	2.04	8.13
30	0	0	260	2.02	8.07
48	0	0	250	2.01	8.05
72	0	0	249	2.01	8.12

Table C.77 Tetrathionate 500 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	7	500	1.84	8.64
24	0	2	499	1.95	8.33
30	0	2	505	1.92	8.44
48	0	3	519	2.00	8.56
72	0	3	523	2.01	8.90

Table C.78 Tetrathionate 1000 ppm, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	1	2	1000	1.95	8.47
24	0	2	1002	2.01	8.70
48	1	3	1016	1.99	8.81
72	3	2	1006	2.08	9.18

Table C.79 Tetrathionate 250 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	2	250	1.93	8.17
6	0	1	254	1.78	7.30
24	0	0	254	1.81	7.99
30	1	0	253	1.81	7.89
48	0	0	244	1.83	7.70
72	0	0	249	1.77	8.02

Table C.80 Tetrathionate 500 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	2	500	1.90	8.73
6	0	3	493	1.91	8.45
24	0	3	505	1.90	8.41
30	0	3	496	1.90	7.71
48	0	2	503	1.92	9.01
72	0	2	503	1.97	9.00

Table C.81 Tetrathionate 1000 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	1	2	1000	2.08
24	1	2	1004	1.91
48	2	3	1003	1.69
72	2	3	1010	1.68

Table C.82 Tetrathionate 250 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	0	250	4.21
24	0	2	255	4.02
30	0	2	253	4.05
48	0	2	251	4.00
72	0	4	249	4.05

Table C.83 Tetrathionate 500 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	0	500	4.14
24	0	0	496	4.02
48	0	0	501	4.09
72	0	0	501	4.12

Table C.84 Tetrathionate 1000 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	4	1000	4.19
24	0	6	1013	4.01
30	0	4	997	4.06
48	0	4	1029	3.99
72	0	2	997	4.02

Table C.85 Tetrathionate 250 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	0	250	3.94	8.11
6	0	1	254	3.98	8.07
24	0	0	255	3.99	8.08
30	0	1	247	3.99	8.07
48	0	3	241	3.96	8.18
72	0	0	245	3.99	8.22

Table C.86 Tetrathionate 500 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	3	500	3.99	8.66
24	0	2	495	4.05	8.53
30	0	3	511	4.06	8.43
48	0	2	506	4.12	8.53
72	0	2	508	4.10	8.30

Table C.87 Tetrathionate 1000 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	1	3	1000	0	3.97	8.50
24	2	4	997	0	4.00	8.53
48	0	2	994	0	3.99	8.60
72	0	6	951	25	4.02	8.74

Table C.88 Tetrathionate 250 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	1	250	3.94	8.09
6	0	1	248	3.88	7.65
24	0	1	243	3.87	8.15
30	0	0	243	3.87	8.34
48	0	0	246	3.88	8.62
72	0	0	246	3.80	8.52

Table C.89 Tetrathionate 500 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	1	3	500	4.11
24	2	1	495	4.01
48	3	1	505	4.00
72	2	0	492	4.00

Table C.90 Tetrathionate 1000 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	1	2	1000	4.11
24	3	3	1007	3.91
48	2	2	993	3.99
72	3	2	995	3.99

Table C.91 Tetrathionate 250 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	0	250	0	6.92
24	0	0	245	0	6.95
48	0	0	250	0	6.85
72	0	0	247	0	6.93

Table C.92 Tetrathionate 500 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	0	0	500	0	6.99
24	0	0	502	0	6.87
48	0	0	491	0	6.92
72	0	0	491	0	6.96

Table C.93 Tetrathionate 1000 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH
0	0	2	1000	7.04
24	0	6	983	6.95
30	0	3	955	6.99
48	0	4	972	6.92
72	0	3	991	6.89

Table C.94 Tetrathionate 250 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	0	250	6.96	8.15
6	0	0	247	6.96	8.24
24	0	1	246	6.95	8.21
30	0	1	246	6.94	8.25
48	0	1	237	6.93	8.26
72	0	3	248	6.93	8.28

Table C.95 Tetrathionate 500 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	2	4	500	6.96	8.14
6	1	2	501	6.96	8.26
24	0	2	499	6.96	8.35
30	0	4	497	6.96	8.39
48	3	2	507	6.96	8.31
72	1	2	519	6.98	8.38

Table C.96 Tetrathionate 1000 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	2	1000	7.00	8.61
24	2	4	998	6.96	8.84
48	2	4	996	6.93	8.70
72	0	4	999	6.93	8.83

Table C.97 Tetrathionate 250 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	2	250	6.99	8.29
30	0	4	250	6.93	8.73
48	6	3	255	6.91	8.34
72	1	3	251	6.90	8.11

Table C.98 Tetrathionate 500 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	2	500	0	6.98	7.99
6	0	0	501		6.96	6.61
24	0	4	500	0	6.94	7.50
30	0	3	504		6.94	7.50
48	3	2	498	0	6.95	7.17
72	2	3	476	0	6.88	6.96

Table C.99 Tetrathionate 1000 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	pH	DO (mg/l)
0	0	1	1000	6.99	8.20
6	1	3	986	6.97	9.15
24	3	3	986	6.95	7.68
30	2	0	994	6.96	8.73
48	5	6	1035		
72	4	10	996	6.95	8.08

Table C.100 Tetrathionate 250 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	1	5	250	0	8.93
24	10	9	237	0	8.87
48	12	10	227	0	8.98
72	13	8	225	0	8.96

Table C.101 Tetrathionate 500 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	4	3	500	0	9.04
6	6	6	491		9.10
24	13	9	469	0	9.02
48	19	11	459	0	8.94
72	22	11	458	0	8.81

Table C.102 Tetrathionate 1000 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	6	5	1000	0	8.94
6	10	7	999		9.12
24	29	14	947	0	9.07
48	35	25	927	0	9.03
72	34	49	906	0	8.97

Table C.103 Tetrathionate 250 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	3	250	0	8.71	7.94
3.5	2	4	247		8.74	8.06
7	3	3	260		8.75	8.13
24	9	5	238	0	8.73	8.20
30	10	5	235		8.72	8.06
48	12	5	228	0	8.74	8.22
72	13	7	221	0	8.74	8.30

Table C.104 Tetrathionate 500 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	2	500	0	8.72	7.93
3.5	4	3	487		8.72	8.12
7	6	3	505		8.72	8.28
24	17	6	485	0	8.70	7.96
48	20	10	462	0	8.66	8.06
72	24	14	459	0	8.67	8.00

Table C.105 Tetrathionate 1000 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	2	4	1000	0	8.72	7.91
3.5	8	6	981		8.70	8.19
7	14	9	967		8.72	8.19
24	28	13	993	2	8.73	7.93
30	29	14	970		8.72	7.93
48	33	23	970	3	8.72	8.24
72	38	29	946	5	8.70	8.29

Table C.106 Tetrathionate 250 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	0	0	250	0	8.81	8.70
7	13	4	239		8.72	8.03
24	25	14	224	0	8.73	7.96
30	32	16	225		8.65	7.87
48	33	24	222	2	8.63	7.92
72	43	32	210	5	8.55	8.19

Table C.107 Tetrathionate 500 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	3	4	500	0	8.96
6	34	16	429		8.81
24	57	40	381	0	8.82
48	82	69	330	0	8.78
72	104	86	281	8	8.77
96	125	104	243	11	8.77

Table C.108 Tetrathionate 1000 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	6	6	1000	0	8.96
6	59	25	909		8.81
24	99	76	788	0	8.81
30	117	88	764		8.77
48	166	131	707	8	8.76
72	229	178	599	14	8.73
96	262	188	463	21	8.74

Thiosalt mixture experiments

Table C.109 Thiosalt mixture 500 ppm each, pH 2, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	500	500	0	2.11
9	509	562	455		2.01
24	486	588	393	7	1.93
30	482	612	342		1.99
48	435	578	470	8	2.00
72	398	552	455	14	2.00

Table C.110 Thiosalt mixture 500 ppm each, pH 2, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	500	500	0	2.12
1	470	490	459		
3	416	496	448	9	2.14
6	378	516	446		2.14
9	387	572	405	12	2.15
24	269	534	445	23	2.16
30	239	534	449		2.18
48	209	511	442	27	2.20
72	182	513	467	33	2.22

Table C.111 Thiosalt Mixture 500 ppm, pH 2, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	500	500	500	0	1.95	8.94
6	355	577	431	0	1.98	8.21
24	277	574	436	11	2.00	7.62
30	285	572	397		2.00	8.09
48	242	523	452	38	2.01	8.44
72	261	537	429	47	2.08	8.29

Table C.112 Thiosalt Mixture 500 ppm, pH 4, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	500	500	9	4.24
6	505	522	511	9	4.06
23	496	501	481	10	4.10
30	504	518	488		4.21
48	502	511	475	10	4.18
72	502	514	475	15	4.18

Table C.113 Thiosalt Mixture 500 ppm, pH 4, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	500	500	500	0	3.99	8.82
24	506	506	472	10	4.05	8.26
30	499	503	479		4.05	8.40
48	511	503	462	7	4.12	8.38
72	509	493	450	16	4.09	8.15

Table C.114 Thiosalt mixture 500 ppm, pH 4, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	500	500	500	0	3.93	8.02
6	507	505	470		3.80	8.82
24	530	483	450	24	3.78	8.94
30	539	482	437		3.94	8.70
48	552	454	430	54	3.82	9.10
72	584	419	419	68	3.78	9.60

Table C.115 Thiosalt mixture 500 ppm, pH 7, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	500	500	0	6.85
6	503	494	521		6.86
25	516	508	513	5	6.86
30	499	498	499		6.91
48	502	510	471	8	6.86
72	506	509	477	13	6.83

Table C.116 Thiosalt mixture 500 ppm, pH 7, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	500	500	0	7.02
6	502	497	464		7.00
24	513	508	453	8	7.00
29	500	503	442		6.97
48	505	501	421	12	7.02
72	509	489	406	20	7.01

Table C.117 Thiosalt mixture 500 ppm, pH 7, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	500	500	500	0	6.96	8.14
6	528	511	479		6.95	7.62
24	571	502	445	30	6.88	8.07
30	542	472	430		6.88	7.78
48	578	455	423	60	6.93	7.04
72	590	409	402	76	6.94	7.90

Table C.118 Thiosalt mixture 500 ppm, pH 9, 4°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH
0	500	500	500	0	9.04
6	530	512	514		9.20
24	516	523	494	7	9.03
30	533	532	493		8.93
48	524	525	490	8	8.98
72	528	528	478	13	8.97

Table C.119 Thiosalt mixture 500 ppm, pH 9, 15°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	500	500	500	0	8.78	7.95
3.5	486	493	482		8.77	8.19
7	514	503	479		8.75	8.07
24	525	520	455	8	8.72	8.16
30	515	539	450		8.62	7.93
48	518	537	436	13	8.61	8.00
72	535	527	444	15	8.55	7.95

Table C.120 Thiosalt mixture 500 ppm, pH 9, 30°C

Time (hrs.)	$S_2O_3^{2-}$ (ppm)	$S_3O_6^{2-}$ (ppm)	$S_4O_6^{2-}$ (ppm)	SO_4^{2-} (ppm)	pH	DO (mg/l)
0	500	500	500	0	8.89	9.10
3.5	537	480	504		8.71	7.74
7	563	483	503		8.64	7.75
24	551	485	441	29	8.49	7.99
30	616	497	423		8.33	7.65
48	662	510	395	51	8.11	7.60
72	728	477	377	74	7.95	8.15