University of Nevada, Reno

Effects of Reduced Sulfur Species on the Recovery of Gold and Silver by Cyanide Leaching

A dissertation submitted in partial fulfillment of the
requirements for the degree of Doctor of Philosophy in
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by

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ABSTRACT

Cyanidation circuits that treat sulfidic ores may contain one or more of the following reduced sulfur species: sulfide (HS^-), polysulfides (S_n^{2-}), thiocyanate (SCN^-), thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$), pentathionate ($S_5O_6^{2-}$), hexathionate ($S_6O_6^{2-}$). The actual speciation of the reduced sulfur species in the circuits will primarily depend on the redox potential, pH, cyanide levels and existing sulfur species in recycled process water, as well as the presence of other reactive metal species. Higher polythionates (i.e. tetra-, penta- and hexa-thionate) present in leach solutions react with cyanide ions rapidly and consume the available cyanide causing lower metal recoveries at cyanide leaching plants. However, if higher polythionate ions could be degraded to trithionate, cyanide consumption would be lowered and metal recoveries would be increased.

The aim of this study is to investigate the possibility of increased gold and silver recoveries and decreased cyanide consumptions by controlling the higher polythionate levels with the addition of sulfite salts to the leach slurries. Experimental results showed that average gold and silver recoveries increased by 13.3% and 28.8%, respectively at 500 ppm NaCN and 300 ppm SO_3^{2-} concentration levels compared to the control experiments where no sulfite was added to the leach slurries. Additionally, higher sulfite concentrations in the leach slurries resulted in lower tetrathionate and thiocyanate and, higher thiosulfate, trithionate and available cyanide concentrations.

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TABLE OF CONTENTS

LIST OF TABLES

.

LIST OF FIGURES

1. INTRODUCTION

Cyanide reacts quantitatively with sulfur, tetrathionate and higher polythionates in aqueous solutions producing thiosulfate, thiocyanate and sulfate. The main consumption of cyanide is probably due to its reaction with higher polythionates. Sulfite (SO_3^{2-}) reacts with higher polythionates and forms trithionate and thiosulfate [1], [2]. The main hypothesis of this research is that the addition of the sulfite salts to the cyanide leach slurries of high sulfur samples would result in transformation of higher polythionates to trithionate which would cause lower cyanide consumptions and higher metal recoveries.

Sodium cyanide (NaCN) is the major reagent used for cyanide leaching. It dissolves in water forming a metal cation and free cyanide ions (CN^-) as presented below [3].

$NaCN \leftrightarrow Na^+ + CN^-$

Gold gives the aurocyanide complex $Au(CN)^{2-}$ when it is leached by cyanide [4].

$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^-$

Silver cyanidation involves the same form of chemical reaction as gold [5].

$4Ag + 8CN^- + O_2 + 2H_2O \rightarrow 4Ag(CN)_2^- + 4OH^-$

Cyanide reacts quantitatively with tetrathionate in aqueous solution producing thiosulfate, thiocyanate and sulfate [6]. Higher polythionates react quantitatively with cyanide and as long as the cyanide is in a stoichiometric excess, all of the polythionates will be converted to thiosulfate ($S_2O_3^{2-}$) and cyanide will be oxidized to thiocyanate (SCN^-) [7], [8].

$CN^- + S_4O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SCN^- + SO_4^{2-} + 2H^+$

$2CN^- + S_5O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + 2SCN^- + SO_4^{2-} + 2H^+$

$3CN^- + S_6O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + 3SCN^- + SO_4^{2-} + 2H^+$

Cyanide ion reacts with thiosulfate forming thiocyanate and sulfite (SO_3^{2-})

$CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$

The reaction of cyanide with trithionate is as follows [8].

$CN- + S_3O_6^{2-} + H_2O \rightarrow SCN^- + SO_3^{2-} + SO_4^{2-} + 2H^+$

Cyanide reacts with sulfur and polysulfide to form thiocyanate,

$8CN^- + S_8 \rightarrow 8SCN$

$CN^- + S_xS^{2-} \rightarrow SCN^- + S_{x-1}S^{2-}$

Existing sulfur species in cyanide solutions interact with each other. Tetrathionate ($S_4O_6^{2-}$) is the initial oxidation product of thiosulfate when pH ≈ 7 [9].

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

Tetrathionate disproportionates to thiosulfate and trithionate ($S_3O_6^{2-}$) [2].

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

Trithionate ion disproportionates at high temperatures when pH > 10 according to the following reaction [10].

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

Presence of polythionates and sulfur increases the cyanide consumption when cyanidation method is used to extract gold/silver from sulfidic ores. By addition of sulfite, tetrathionate reacts quantitatively with sulfite and forms trithionate and thiosulfate [1].

$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-}$

Higher polythionates also undergo similar reactions [2].

$S_5O_6^{2-} + 2SO_3^{2-} \rightarrow S_3O_6^{2-} + 2S_2O_3^{2-}$

$S_6O_6^{2-} + 3SO_3^{2-} \rightarrow S_3O_6^{2-} + 3S_2O_3^{2-}$

Elemental sulfur could also be treated by sulfite addition [11].

$S + SO_3^{2-} \rightarrow S_2O_3^{2-}$

Some refractory gold plants that employ bio oxidation as the sole pretreatment step experience excessively high levels of cyanide consumption where values as high as 30 kg NaCN/ton concentrate have been reported. The high cyanide consumption increases operating cost as polythionates represent a drawback to the recovery of gold and silver by cyanidation. The present work studies remediation of the reduced sulfur effects on cyanide consumption and metal recoveries. Throughout the experimental work of this study, cyanide bottle roll tests were conducted to assess the metal recoveries from flotation tailings samples by cyanide leaching. Bottle roll experiments were conducted under alkaline conditions with the addition of only cyanide; cyanide and tetrathionate; and cyanide, tetrathionate and sulfite salts. Leach solutions were analyzed by high performance liquid chromatography (HPLC) with ultraviolet (UV) absorbance detection system, atomic absorption spectrometer (AAS), and cyanide analyzer. The wash solutions and solid residues were analyzed for their gold, silver and copper contents by using fire assaying, multi acid digestion and AAS methods.

2. LITERATURE SURVEY

2.1 ELEMENTAL SULFUR AND OTHER SULFUR SPECIES

Sulfur (S) usually forms as cyclic octatomic molecules with the chemical formula S_8. Sulfur reacts with all elements except for gold, tellurium, platinum, iridium and noble gases. The most common formation of the sulfur is as sulfide and sulfate, but sulfur also occurs naturally as an element. The sulfur and oxygen atom have the same number of valence electrons. For that reason, S_2 and S_3 have similar physical and chemical properties as O_2 and O_3 [12].

Elemental sulfur also forms by sulfide decomposition in aqueous solutions or during pressure oxidation in mineral processing plants. During the cyanidation process, elemental sulfur in aqueous solutions reacts with cyanide to form various sulfur species. Thus, formation of the elemental sulfur should be avoided to decrease cyanide consumption in cyanide leaching plants.

Sulfites are compounds that contain sulfite ion, SO_3^{2-} [13]. Sulfites may exist as different ions, such as bisulfite HSO_3^{2-} or metabisulfite $S_2O_5^{2-}$.

Sulfides are the compounds that contain the divalent inorganic anion of sulfur, S^{2-} and they form when hydrogen sulfide loses its proton in its structure [14]. One of the most common sulfide compounds is Na_2S. Generally, sulfides are classified as strong base.

Sulfates are the salts of sulfuric acid and contains the polyatomic ion SO_4^{2-}. Sulfates can also form by the oxidization of metal sulfides [15]. Most of the sulfate salts are molecularly or completely soluble in water.

2.2 GOLD AND SILVER BEARING SULFIDE ORES

Sulfide minerals are the inorganic compounds that contain sulfur with one or more elements. Below the oxide formation, at deeper regions of the ore bodies, most of the gold and silver deposits form as sulfides. Gold and silver recovery from oxide ores can be as high as +90% by cyanidation whereas the recoveries from sulfide ores are very low, generally less than 50%, by this method. This makes many precious metal deposits unprofitable to mine unless different recovery methods are applied. Figure 1 shows the gold grains associated with iron oxide within an oxide ore sample.

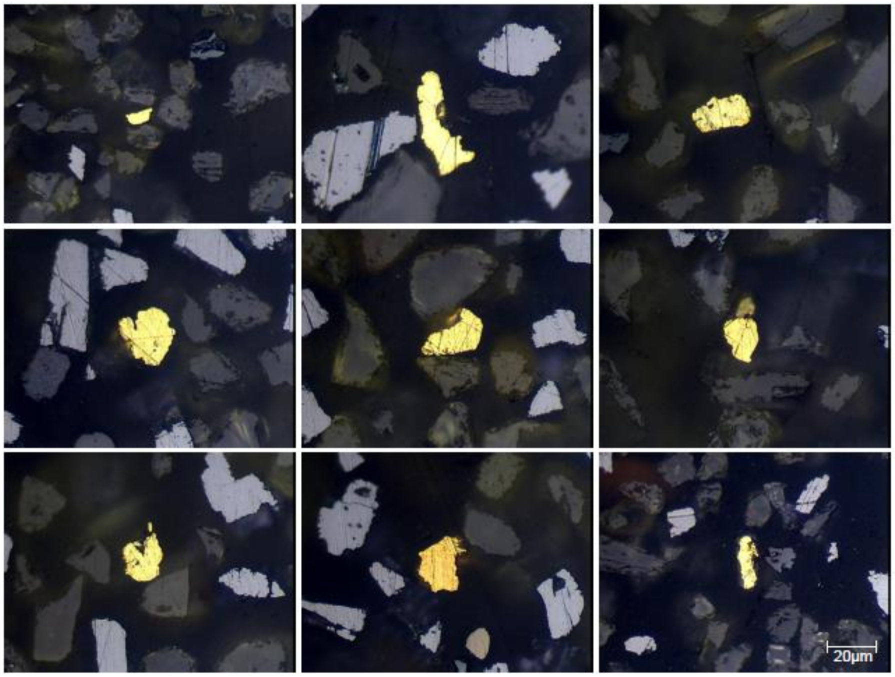


Figure 1. Gold Association with FeO_x

Example of electrum and some other gold associations with sulfide minerals are shown in Figure 2. The figure shows the following associations in clockwise direction, 1st - Electrum (Au,Ag), 2nd - Native Gold attached to Chalcopyrite ($CuFeS_2$), 3rd - enclosed in pyrite (FeS_2) and 4th – enclosed in quartz.

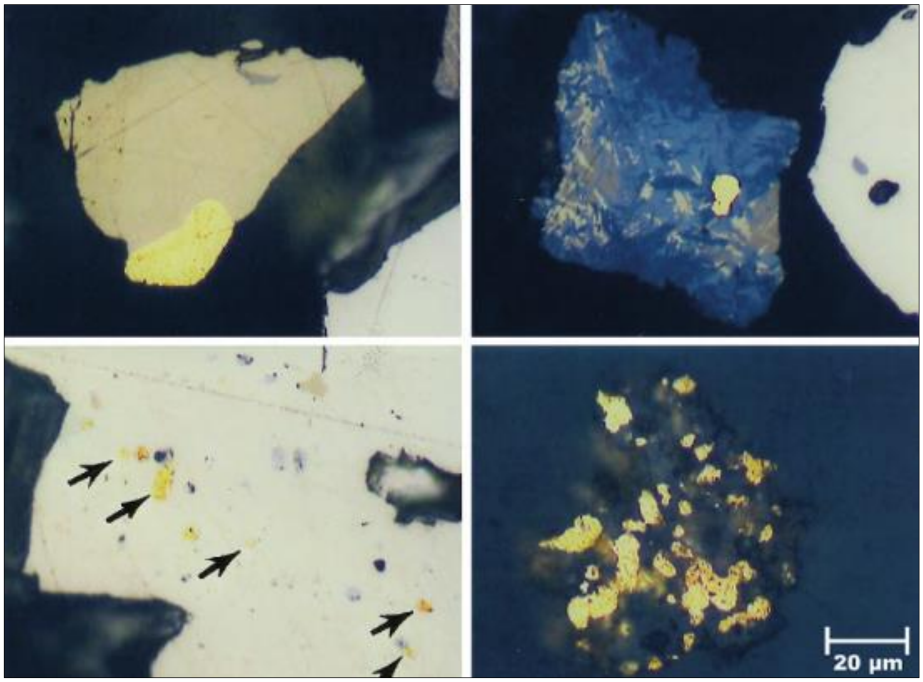


Figure 2. Gold Association with Sulfide Minerals [16]

The concentrations of gold and silver are generally associated with sulfide minerals [17]. The main constituent of sulfide ores are iron sulfides, copper sulfides, arsenic sulfides and antimony sulfides. Silver generally occurs as argentite (Ag_2S) and gold may occur as invisible inclusions within the sulfide minerals [18]. The gold content of some sulfide minerals is presented in Table 1 [16].

Mineral	Formula	Mineral Au (ppm)
Iron sulfides		
Pyrite	FeS_2	<0.1–8,800
Marcasite	FeS_2	<0.1–31
Pyrrhotite	$Fe_{(1-x)}S$	<0.1–5
Arsenic minerals		
Arsenopyrite	FeAsS	<0.2–17,000
Loellingite	$FeAs_2$	<0.2–17,000
Tennantite	$Cu_{12}As_4S_{13}$	<0.2–72
Enargite-Luzonite	Cu_3AsS_4	<0.3–62
Gersdorffite	NiAsS	<0.1–5
Realgar	As_4S_4 or AsS	<0.1–4
Orpiment	As_2S_3	<0.1–3
Copper sulfides		
Chalcopyrite (synthetic)	$CuFeS_2$	<0.1–7
Bornite (synthetic)	Cu_5FeS_4	<0.1–14
Covellite	CuS	<0.1–74
Chalcocite	Cu_2S	<0.1–44
Antimony sulfides		
Tetrahedrite	$(Cu,Fe)_{12}Sb_4Sb_{13}$	<0.2–59
Stibnite	Sb_2S_3	<0.1

Table 1. Gold Contents of Some Sulfide Minerals

2.2.1 IRON SULFIDES

Iron sulfides refer to the chemical compounds composed of iron and sulfur. Pyrite (FeS_2) is one of the most common sulfide minerals. Pyrite can be found in igneous, sedimentary, metamorphic rocks and in hydrothermal mineral deposits. Gold may occur in pyrite as inclusions. Another iron sulfide mineral, marcasite has the same chemical formula as pyrite, but a different crystalline structure. Pyrite has an isometric crystal structure whereas marcasite has orthorhombic structure which causes them to have different physical properties from each other. The other common iron sulfide mineral is pyrrhotite ($Fe_{(1-x)}S$, x=0 to 0.2). It has a monoclinic crystal system with hexagonal polytypes. Pyrrhotite is mostly found in igneous rocks.

In sediment-hosted disseminated pyritic Carlin type deposits gold can be found up to 0.40% by weight [19]. Flotation and roasting are two main processing methods applied for the recovery of the precious metals from iron sulfides.

2.2.2 COPPER SULFIDES

Gold and silver are recovered as a byproduct from copper-gold ore deposits. Higher grade copper sulfide ores can be processed by smelting while lower grade ores can be processed by hydrometallurgical methods. The most important commercial processing method for recovering value from copper-gold-silver-pyrite ores is flotation.

Chalcopyrite ($CuFeS_2$) is the most common copper sulfide mineral [20]. Chalcopyrite has a tetragonal crystal system and generally occurs in hydrothermal veins, stockworks and disseminations.

Other important copper sulfide minerals are bornite (Cu_5FeS_4), chalcocite (Cu_2S) and covellite (CuS). Bornite, chalcocite and covellite have orthorhombic, monoclinic and hexagonal crystal systems, respectively [21]. Bornite is generally found in porphyry copper deposits and generally replaced by chalcocite and covellite formed under hydrothermal conditions.

2.2.3 ARSENIC SULFIDES

Arsenic may substitute sulfur into the isometric crystal structure of pyrite forming arsenopyrite (FeAsS). Arsenopyrite and arsenic-rich varieties of pyrites also hosts gold [22]. Gold-aresenopyrite deposits are highly saturated with finely crystalline arsenopytite. Gold occurs as both free and refractory in gold-arsenopyrite deposits [23]. When arsenopyrite forms in association with pyrite, gold assay grade in arsenopyrite is higher than in pyrite [24]. Arsenic sulfide minerals form complex reducing compounds and consume dissolved oxygen in alkaline solutions causing low gold dissolution rates.

Orpiment is another arsenic sulfide mineral with the formula As_2S_3 and monoclinic crystal system. More than thirty percent of gold can be adsorbed from sulfide solutions by orpiment depending on the pH of a solution. Orpiment will adsorb almost all the gold present in the solution if the solution pH goes below 4.5 [24].

Realgar (As_2S, α-As_4S_4) is another arsenic sulfide mineral, occuring with other arsenic and antimony minerals in low-temperature hydrothermal veins [21]. Realgar has a monoclinic crystal system and is found associated with several sediment hosted gold deposits.

2.2.4 ANTIMONY SULFIDES

Antimony sulfide deposits may have gold associated with antimony minerals or antimony may independently occur within the deposit [20]. One of the major cyanidation problems associated with this type of deposit is that antimony dissolves in cyanide solution and forms antimonates retarding the gold dissolution [25]. Stibnite (Sb_2S_3), the sulfide of antimony, is commonly found in epithermal deposits. Stibnite has orthorhombic crystal structure. Another antimony sulfide group mineral is aurostibnite ($AuSb_3$). It has isometric crystal structure and generally occurs in hydrothermal gold-quartz veins [26].

2.3 CYANIDE NOMENCLATURE

2.3.1 CYANIDE SPECIES

Cyanide is very reactive and easily forms organic compounds and metal cyanide complexes. The stability of these complexes depends on the metal and its valence number. The formation of cyanide complexes also depends on pH, temperature, presence of trace metals and sulfur compounds. Determination of cyanide species is dependent on the relative strength of metal complexes that it forms. Cyanide complexes are classified into three major groups; total cyanide, weak acid dissociable (WAD) cyanide and free cyanide. Available cyanide is the sum of the free cyanide and WAD cyanide complexes which dissociates under moderate acidic conditions (pH 4-6) [27]. Total cyanide is the sum of the strong metal-cyanide complexes ($Fe(CN)_6^{2-}$, $Co(CN)_6^{4-}$, $Au(CN)_2^{-}$, WAD and free cyanide. Strong-metal cyanide complexes dissociates under strong acidic conditions.

2.3.1.1 FREE CYANIDE

Free cyanide is the sum of the cyanide ion CN^- and hydrogen cyanide HCN in a solution. The proportion of the CN^- and HCN in the solutions is directly influenced by the pH of the solution. At pH 7 or less free cyanide consists primarily as HCN [28]. Hydrogen cyanide is an organic compound with a linear molecule and triple bond between carbon and nitrogen [29]. It is a weak acid and its acid dissociation constant is 2.1×10^{-9} mol dm^{-3} [30].

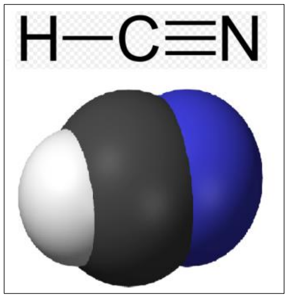


Figure 3. Valance Bond Structure and Space-Filling Model of HCN Ion.

Cyanide is a monovalent anion and forms by triple bonding of a carbon atom to a nitrogen atom. It is a deprotonated HCN molcecule.

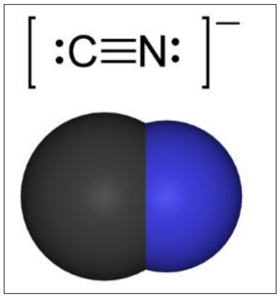


Figure 4. Valance Bond Structure and Space-Filling Model of CN^- Ion.

2.3.1.2 WEAK ACID DISSOCIABLE (WAD) CYANIDE

WAD cyanide is the metal cyanide complexes that are formed with Zn, Cd, Cu, Hg, Ni, Ag that dissociate under weak acid conditions where pH is 4 to 6. WAD cyanide species are also divided into two major groups weak metal-cyanide, i.e. $Zn(CN)_2$, $Cd(CN)_3^-$, and moderately strong metal-cyanide complexes, $Cu(CN)_2^-$, $Ag(CN)_2^-$.

The general representation of these metal-cyanide complex formations is represented by the following reaction [31],

$$M^{x+} + yCN^- \leftrightarrow [M(CN)_y]^{(y-x)-} \qquad (1)$$

Where $[M(CN)_y]^{(y-x)-}$: Metal-cyanide complex

M^{x+} : Metal ion

During the measurement of the free cyanide in the solutions, the selected analysis method should not affect the stability of the WAD cyanide complexes since any interference with these complexes may result in a higher free cyanide quantification than the actual results [32].

2.3.2 CHEMISTRY OF CYANIDE IN SOLUTIONS

Sodium cyanide (NaCN) is the major reagent used for cyanide leaching. It dissolves in water forming a metal cation (Na^+) and free cyanide ion (CN^-) [33].

Hydrolyzed cyanide ions form hydrogen cyanide (HCN) and increase pH of the solution by forming hydroxyl (OH^-) ions. Hydrogen cyanide dissociates in water to hydrogen and cyanide ions and the direction of this reaction is directly dependent on the pH value of the solution [34]. Total cyanide exists as half hydrogen cyanide and half free cyanide ions at pH 9.3 [35].

Figure 5 shows the speciation of cyanide and hydrogen cyanide in aqueous solution as a function of pH.

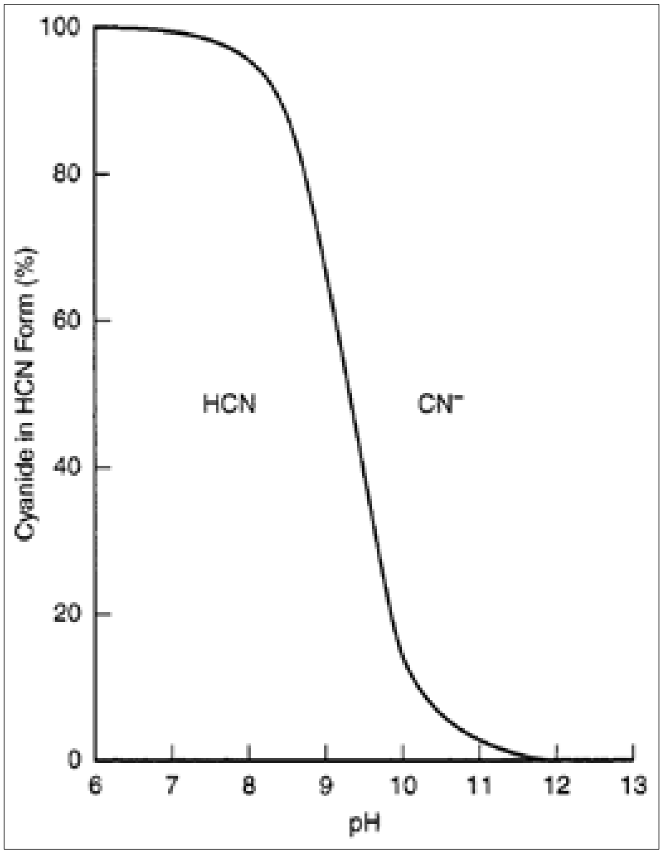


Figure 5. Effect of pH on Formation of CN^- and HCN [18]

The hydrolysis of cyanide ions and equilibrium constants are shown in Equation 2 [36],

$CN^{-}_{(aq)} + H_2O_{(l)} \leftrightarrow HCN_{(aq)} + OH^{-}_{(aq)}$ (2)

$$K_b = \frac{K_w}{K_a} = \frac{[H_3O^+]\,[OH^-]}{K_a} = \frac{10^{-14}}{K_a} = 1.6\ x\ 10^{-5}$$

The dissociation reaction of hydrocyanic acid in water and dissociation constant of this reaction is presented in Equation 3 [37],

$HCN_{(aq)} + H_2O_{(l)} \leftrightarrow H^{+}_{(aq)} + CN^{-}_{(aq)}$ (3)

$$Ka = \frac{[H^+]\,[CN^-]}{[HCN]} = 6.2 \text{ x } 10^{-10}$$

Free cyanide ions compete with OH^- and H^+ during its reaction with water. For this reason, the pH of the cyanide solutions will define the amount of free cyanide and HCN formed during the Reactions 2 and 3.

At pH 12 hydrogen cyanide completely dissociates in water and exists as free cyanide ions [38]. Above this pH value, the total cyanide exists as free cyanide ions.

Hydrogen cyanide and free cyanide can be oxidized by oxygen to form cyanate (CNO^-) during leaching. Cyanate formation has adverse effects on recovery since it does not dissolve gold and also decreases free cyanide concentration in the solution. CNO^- forming reactions are shown in Equations 4 and 5 [39].

$4HCN + 3O_2 \leftrightarrow 4CNO^- + 2H_2O$ (4)

$3CN^- + 2O_2 + H_2O \leftrightarrow 3CNO^- + 2OH^-$ (5)

The Eh – pH diagram for the CN – H_2O system is given in Figure 6. In this system, the cyanide ion concentration is known as 10^{-3} kmol/m^3.

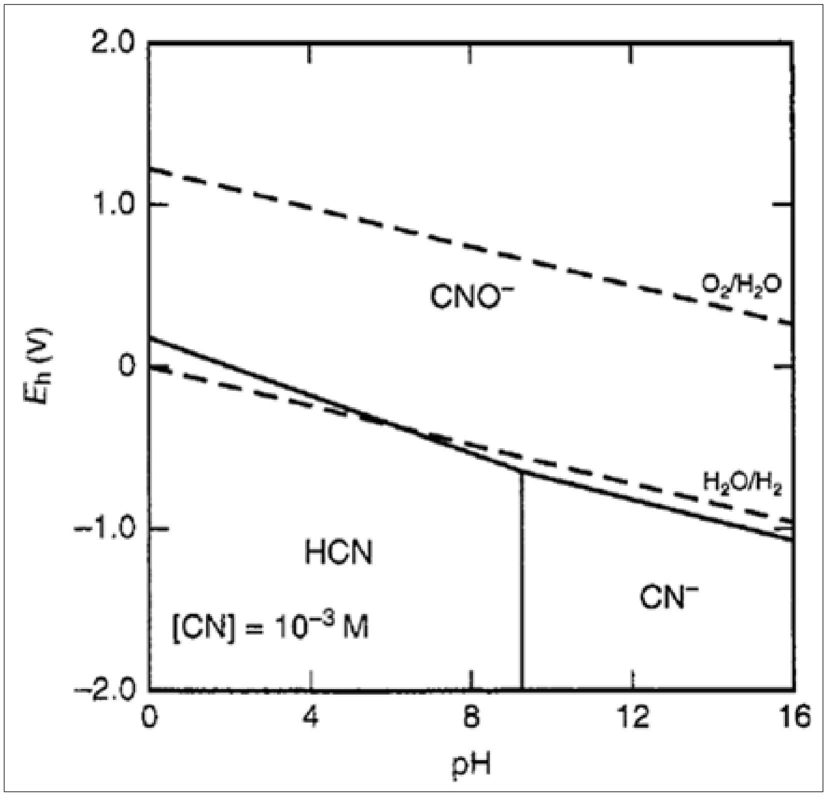


Figure 6. CN – H_2O System E_h – pH Diagram at 25 C° [40]

Thiocyanate (SCN^-) is another common cyanide species that forms when cyanide reacts with sulfur containing species. Thiocyanate may also be formed by the reaction of polysulfides and thiosulfates with cyanide ion [41].

$S_x^{2-} + CN^- \leftrightarrow S_{(x-1)}^{2-} + SCN^-$ (6)

$S_2O_3^{2-} + CN^- \leftrightarrow SO_3^{2-} + SCN^-$ (7)

At the gold leaching operations, thiocyanate formation causes higher cyanide and oxygen consumption in leach tanks which results in lower metal recoveries.

There are several different cyanide forms that may occur in their solutions. These cyanide species can be formed based on oxidation state of carbon atom on their complexes. The oxidation state for cyanide, cyanogen, cyanate and thiocyanate are (II), (III), (IV), (IV), respectively [42].

2.3.3 CYANIDE ANALYSIS METHODS

There are different methods developed by the United States Environmental Protection Agency (USEPA), American Water Works Association (AWWA), American Society for Testing and Materials (ASTM) and International Standards Organization (ISO). These methods include,

- Available Cyanide, USEPA Method OIA-1677-09 - This method is useful to determine the aquatic free cyanide to establish at a given pH and temperature [43].

- Recovery of Aqueous Cyanides by Extraction from Mine Rock and Soil, ASTM D 7572-11a - This method is applied for collection, extraction and preservation of extracts from mine rock and soil samples for the analysis of cyanide extracts [44].

- Standard Test Methods for Cyanides in water, ASTM D 2036-09 - This method determines cyanides in water. It covers four test methods for total cyanides after distillation, cyanides amenable to chloration, WAD cyanides, cyanides amenable to chlorination without distillation [45].

- Total Cyanide, ASTM Methods D 7511-09e2 - This method is used for determining total cyanide in liquids by using segmented flow analysis and flow injection analysis [46].

- Methods for International Cyanide Management Code, ASTM D 7728-11 - This guide is generally used for the gold leaching process and environmental monitoring [47].

- Aquatic Free Cyanide, ASTM Method D 7237-10 - This method is used to determine the concentration of free cyanide in liquids by applying flow injection analysis utilizing gas diffusion separation and amperometric detection [48].

- Total Cyanide, ASTM Method D 7284-08 - This method uses a micro-distillation process followed by flow injection analysis with gas diffusion separation and amperometric detection [49].

- Total Cyanide, ISO-14403:2012 – This method determines total and free cyanides in liquids by using continuous flow and flow injection analysis [50].

2.3.3.1 INTERFERENCES

Samples that contain sulfur species, nitrite and oxidizing agents may interfere with cyanide analysis during the acid distillation step [51]. Sulfides form thiocyanate ($SCN^–$) by reacting with the free cyanide in solutions causing lower cyanide detections than actual. This happens mainly because thiocyanates decompose by oxidation of sulfur compounds during distillation and react with cyanide in the solution. Sulfides may also cause higher cyanide detections than the actual concentration by distillation and reaction of the volatilized sulfides with colorimetric reagents. Thiosulfate ($S_2O_3^-$) salts may react during distillation and form cyanate (OCN^-) compounds causing lower cyanide detections than actual. Samples containing sulfites form H_2SO_3 and forms SO_2 gas which absorbed in the NaOH scrubber and form Na_2SO_3. This causes the scrubber absorbing solution to contain SO_3^{2-}, CN^-, and dissolved oxygen. CN^- is oxidized to OCN^- by the sulfite and dissolved oxygen resulting in lower cyanide measurements than actual. Oxidizing agents decompose cyanides during the acid distillation step and will cause lower than actual cyanide measurement results.

2.4 CHEMISTRY OF METAL SULFIDES DISSOLUTION IN CYANIDE SOLUTIONS

Metal sulfides dissolve in cyanide solutions during both homogenous and heterogeneous phases. Kinetic data may provide insight on solubility products of the metal sulfides; however, the calculation of the constant correctly is difficult because of the simultaneous complexing of the metal cation by the existing ions and functional groups in the leach solutions.

The general dissolution of the metallic sulfides is presented by Equation 8 [52],

$$Me_a^{z+}S_b^{2-} \leftrightarrow aMe^{z+} + bS^{2-} \tag{8}$$

Me : Metal

S : Sulfur

a, b : Stoichiometric coefficients

z : Cation charge value

The solubility product equation is defined in Equations 9 and 10,

$$K_{sp} = (M_{Me^{z+}})^a \cdot (M_{S^{2-}})^b \cdot \gamma^{\pm\,(a+b)} \tag{9}$$

$$\gamma^{\pm\,(a+b)} = \gamma^a_{Me^{z+}} \cdot \gamma^b_{S^{2-}} \tag{10}$$

M : molarity

γ : mean activity coefficient

The solubility of the metal sulfides also depends on the pH of the leach solutions. The hydrolyzation of the sulfur ions during the dissolution occurs and affects the pH of the solution as follows,

$S^{2-} + H_2O \leftrightarrow HS^- + OH^-$ (11)

$$K_{HS^-} = \frac{[HS^-]}{[S^{2-}][H^+]} \quad (12)$$

$HS^- + H^+ \leftrightarrow H_2S_{(aq)}$ (13)

$$K_{H_sS} = \frac{[H_2S]}{[HS^-][H^+]} \quad (14)$$

During the cyanidation of the metal sulfides, multiple cyanide complexes are formed. The simplified representation of these interaction between the dissolved metal sulfides and cyanide ion are presented below,

$FeS_2 + 8CN^- \leftrightarrow Fe(CN)_6^{4-} + 2SCN^- + 2e^-$ (15)

$FeS + 7CN^- \leftrightarrow Fe(CN)_6^{4-} + SCN^- + 2e^-$ (16)

$CuFeS_2 + 10\ CN^- \leftrightarrow Fe(CN)_6^{4-} + Cu(CN)_2^- + 2SCN^- + 3e^-$ (17)

$Cu_2S + 5CN^- \leftrightarrow 2Cu(CN)_2^- + SCN^- + 2e^-$ (18)

$ZnS + 3CN^- \leftrightarrow Zn(CN)_2 + SCN^- + 2e^-$ (19)

$S_o + CN^- \leftrightarrow SCN^-$ (20)

The solubility of each sulfide mineral in cyanide solutions differs in the range of completely soluble to very low soluble. Table 2 shows most common sulfide minerals and their solubility in cyanide solution [4].

	Mineral	Composition	% Dissolved in 24 hrs.
Iron Minerals	Pyrrhotite	FeS	Readily
	Pyrite	FeS_2	Sparingly
Zinc Minerals	Sphalerite	ZnS	18
Copper Minerals	Chalcocite	Cu_2S	90
	Bornite	$FeS.2Cu_2S.CuS$	70
	Chalcopyrite	$CuFeS_2$	5.6
Arsenic Minerals	Orpiment	As_2S_3	73
	Realgar	As_2S_2	9
	Arsenopyrite	FeAsS	21
Lead Minerals	Galena	PbS	Soluble
Antimony	Stibnite	Sb_2S_3	21

Table 2. Solubility of Most Common Sulfide Minerals in Cyanide Solutions

The presence of sulfide minerals in gold and silver ores causes high cyanide and oxygen consumption during leaching, and consequently causes low metal recoveries.

Cyanidation is negatively affected by the presence of free sulfur or sulfide minerals present in the ore. When the ore is wetted in the presence of oxygen, sulfides form sulfuric acid which reacts with cyanide resulting in higher cyanide consumption and formation of poisonous HCN gas under low pH conditions. This will require an increase in addition of the lime to the process to control the pH and avoid volatilization of HCN. Substances that destroy the cyanide salts are called cyanicides and they affect gold cyanidation by forming stronger cyanide complexes than gold, forming new radicals and adsorbing CN^- radicals by consuming dissolved oxygen [16].

The solubility of the common sulfide minerals in cyanide solutions in decreasing order is pyrrhotite, marcasite, and pyrite. Solution pH is the main affecting parameter for the solubility of these minerals [53]. Figure 7 shows the effect of different sulfide minerals on gold cyanide leaching.

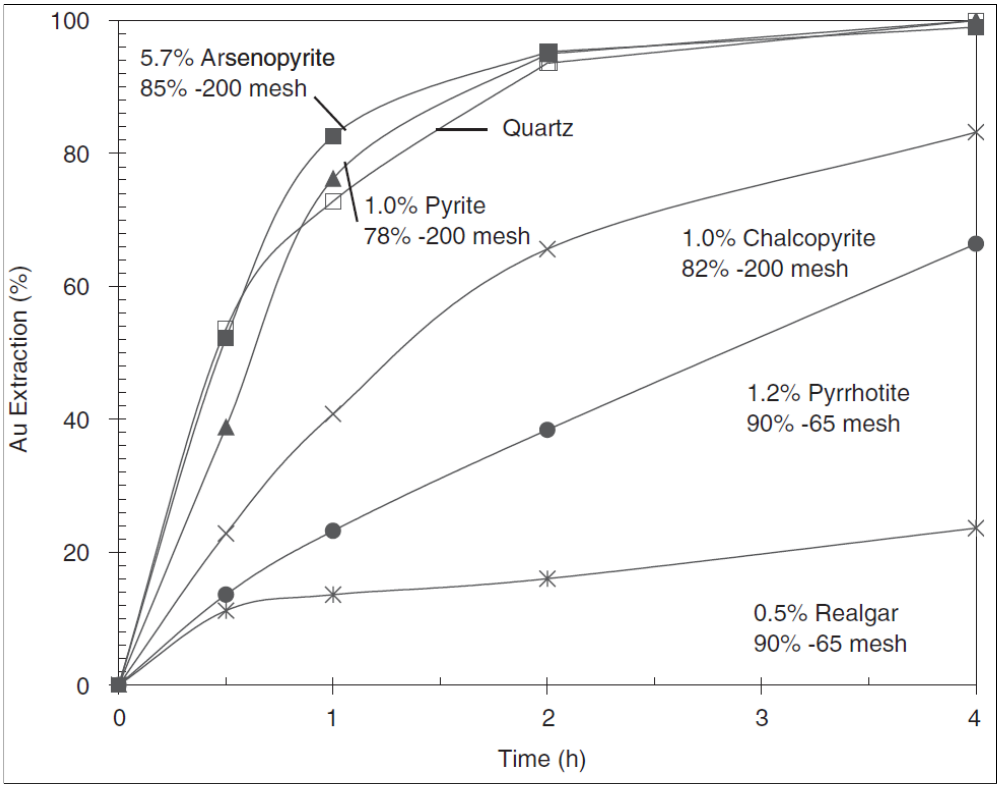


Figure 7. Effect of Presence of Sulfide Minerals on Gold Recovery (Au: 25 g/t, 500 mg/L NaCN, pH 11.5, 8 ppm O_2) [54]

Addition to the sulfide minerals presented in Figure 7, according to another study, the reactivity of the following sulfide minerals with cyanide in decreasing order is stibnite, orphiment, realgar and arsenopyrite [55].

2.5 CHEMISTRY OF REDUCED SULFUR SPECIES IN CYANIDE SOLUTIONS

Sulfidic ores that are treated in cyanidation circuits may contain one or more of the following sulfur species:

Sulfide (HS^-), Disulfide (S_2^{2-}), Polysulfides (S_n^{2-}), Thiocyanate (SCN^-), Thiosulfate ($S_2O_3^{2-}$), Trithionate ($S_3O_6^{2-}$), Tetrathionate ($S_4O_6^{2-}$), Pentathionate ($S_5O_6^{2-}$), Hexathionate ($S_6O_6^{2-}$), Sulfite (SO_3^{2-}).

Thiocyanate is formed by the Reactions 21 and 22 of sulfur or thiosulfate with cyanide ion,

$$8CN^- + S_8 \rightarrow 8\ SCN^- \qquad (21)$$

$$CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-} \qquad (22)$$

At high pH, reduced products of sulfur convert cyanide ion to thiocyanate ion rapidly. This presence of sulfide in the slurry will cause low cyanide recoveries due to the formation of thiocyanate.

The stable E_h-pH diagram for the SCN-H_2O system for the 0.5 and 0.005 M thiocyanate concentrations at 25 °C is presented in Figure 8 [56].

Due to the mutual interactions of the reduced sulfur species, a specific cyanidation solution will not have all the anions presented in the beginning of this section. The formation of the reduced sulfur species will directly be affected by the redox potential, pH, cyanide levels, cyanide species and different reactive species that formed in the solution.

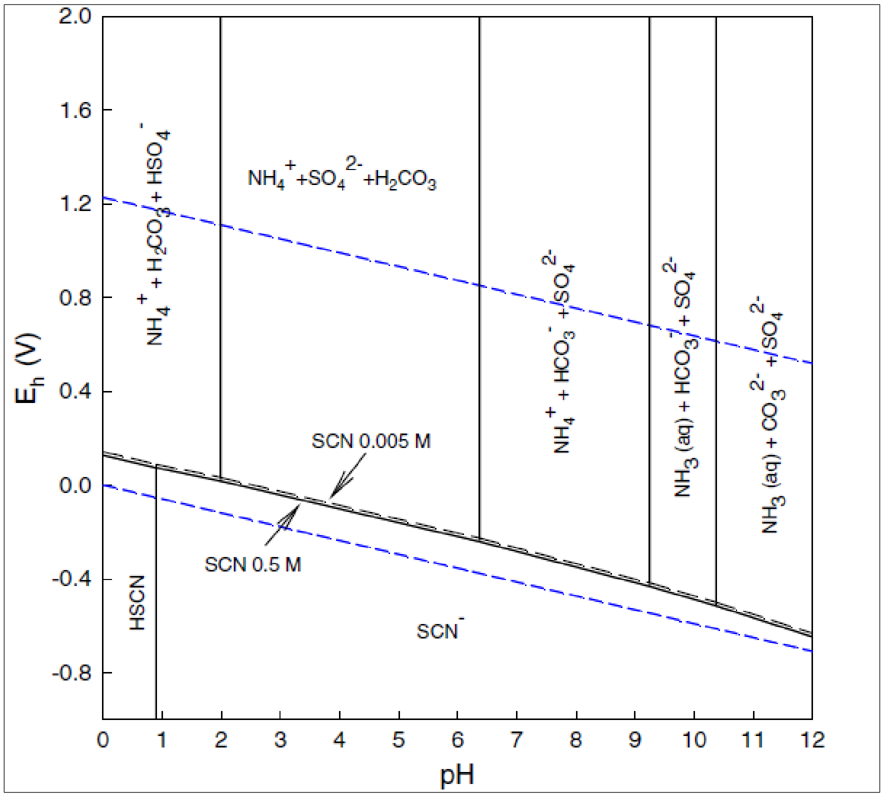


Figure 8. Eh-pH Diagram for the SCN-H_2O System for the 0.5 and 0.005 M Thiocyanate Concentrations at 25 ^{o}C [57]

Cyanide reacts with oxidized sulfur species and produces thiocyanate with the presence of an oxidizing agent in solution [58]. Dissolved oxygen in leach solutions is the primary cause of the oxidation of the reduced sulfur species, e.g. polysulfides, sulfites, thiosulfates, and react with cyanide to form thiocyanate with the presence of oxygen [59]. Figure 9 summarizes all the reactions of the oxygenation of sulfide to form thiocyanate.

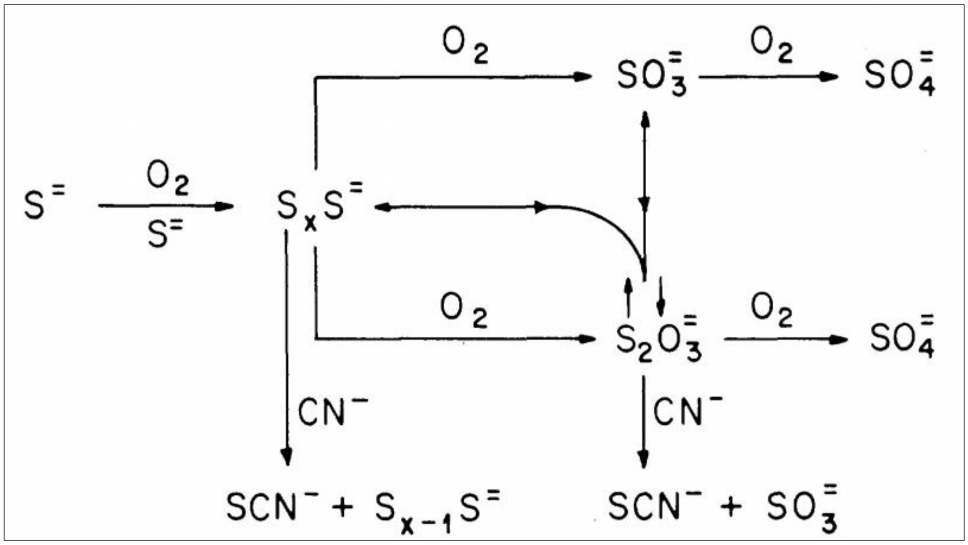


Figure 9. Reactions of Cyanide with Reduced Sulfur Species yielding Thiocyanate in Aqueous Solutions [60]

The thiocyanate formation kinetics should also be analyzed based on sulfide oxygenation pathways if a system initially contains cyanide and sulfide. If there is 10^{-3} M or more sulfide in an alkaline solution, polysulfide may exist as a sulfide oxidation product and the formed polysulfide can react rapidly with cyanide to form thiocyanate.

Aqueous sulfide in leach solutions oxidizes to sulfur and forms polysulfide by the following reaction [58],

$$4HS^- + O_2 \leftrightarrow 2S_2^{2-} + 2H_2O \qquad (23)$$

Polysulfide formed in Equation 23 reacts with cyanide ion and forms thiocyanate and another polysulfide as shown in Equation 24,

$S_xS^{2-} + CN^- \leftrightarrow S_{x-1}S^{2-} + SCN^-$ (24)

Additionally, based on the diagram in Figure 9, after the sequence of the following reactions, thiocyanate forms by the initial oxidation of sulfide sulfur to sulfite [61].

$2S^{2-} + 3O_2 \leftrightarrow 2SO_3^{2-}$ (25)

$SO_3^{2-} + S_2^{2-} \leftrightarrow 2S_2O_3^{2-} + S^{2-}$ (26)

$S_2O_3 + CN^- \leftrightarrow SCN^- + SO_3^{2-}$ (27)

The formed sulfite in Equation 25 reacts with polysulfide in leach solutions and forms thiosulfate. And thiosulfate reacts with free cyanide forming thiocyanate and sulfite, as shown in Equation 27.

The reaction of cyanide with trithionate is as follows but reaction kinetics are very slow at temperatures below 40°C [62].

$CN^- + S_3O_6^{2-} + H_2O \leftrightarrow SCN^- + SO_3^{2-} + SO_4^{2-} + 2H^+$ (28)

Cyanide ion reacts with tetrathionate in aqueous solutions and forms thiosulfate, thiocyanate and sulfate. Furthermore, the reaction generates two moles of hydrogen ions and decreases the leach solution pH. Overall reaction is shown by the below equation [63],

$CN^- + S_4O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + SCN^- + SO_4^{2-} + 2H^+$ (29)

Higher polythionates also react quantitatively with cyanide [64], [65].

$$2CN^- + S_5O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + 2SCN^- + SO_4^{2-} + 2H^+ \quad (30)$$

$$3CN^- + S_6O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + 3SCN^- + SO_4^{2-} + 2H^+ \quad (31)$$

Optimum pH ranges for the reactions of tetrathionate, pentathionate ($S_5O_6^{2-}$) and hexathionate ($S_6O_6^{2-}$) with cyanide are 8.3 - 12.1, 8.0 - 8.8 and 7.8 - 8.9, respectively. As long as the cyanide is in a stoichiometric excess and once the reactions 29 to 31 go to completion, all the polythionates are converted to thiosulfate ($S_2O_3^{2-}$) and free cyanide is oxidized to thiocyanate (SCN^-).

2.6 MUTUAL INTERACTIONS BETWEEN REDUCED SULFUR SPECIES

Another source of the formation of complex molecules of polythionates is by the reaction of H_2S and SO_2 [66]. The transformation of the formed polythionate species occur through the redox reactions, bimolecular displacements and hydrolysis reactions [67]. Polythionates have stability areas between sulfide and sulfate as presented in the following Eh-pH diagram for the metastable S-H_2O system (S = 1 M). The S-H_2O system without thiosulfate is positioned to show an increase in tetrathionate ($S_4O_6^{2-}$) area.

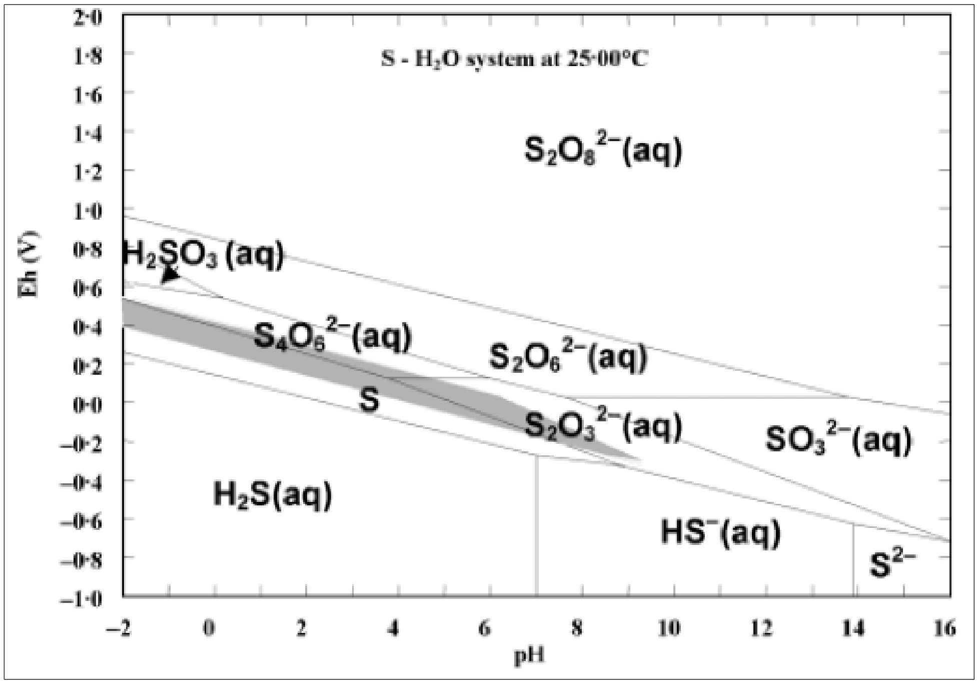


Figure 10. Stability of Intermediate Sulfur Species in the Absence of Sulfate Ion [68]

Polythionates ($S_xO_6^{2-}$, x=3-6) and thiosulfate ($S_2O_3^{2-}$) are important intermediate species in the redox transformations of the sulfur compounds.

Trithionate ion disproportionates at high temperatures and pH 10 according to the following reaction [69],

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^{+} \tag{32}$$

Tetrathionate ($S_4O_6^{2-}$) will undergo disproportionation reaction in neutral solutions to trithionate and pentathionate [9].

$$2S_4O_6^{2-} \leftrightarrow S_3O_6^{2-} + S_5O_6^{2-} \tag{33}$$

In alkaline solutions where pH>10, tetrathionate disproportionate to thiosulfate and tritionate,

$$4S_4O_6^{2-} + 6OH^- \leftrightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad (34)$$

Pentathionate also disproportionates to thiosulfate in alkaline solutions by the following equation,

$$2S_5O_6^{2-} + 6OH^- \leftrightarrow 5S_2O_3^{2-} + 3H_2O \qquad (35)$$

Sulfite ions prevent formation of passivating layer of colloidal sulfur on the precious metal surfaces by attacking the sulfur-sulfur bonds and helps decreasing tetrathionate and higher polythionate concentrations in leach solutions [70]. An increase in SO_3^{2-} ion molarity causes tetrathionate, pentathionate, hexathionate ion degradation to thiosulfate and trithionate according to the following reactions [71], [72].

$$S_4O_6^{2-} + SO_3^{2-} \leftrightarrow S_2O_3^{2-} + S_3O_6^{2-} \qquad (36)$$

$$S_5O_6^{2-} + 2SO_3^{2-} \leftrightarrow 2S_2O_3^{2-} + S_3O_6^{2-} \qquad (37)$$

$$S_6O_6^{2-} + 3SO_3^{2-} \leftrightarrow S_3O_6^{2-} + 3S_2O_3^{2-} \qquad (38)$$

2.7 CHEMISTRY OF GOLD AND SILVER DISSOLUTION IN CYANIDE AND THIOSULFATE

Gold is the only metal that is generally found in metallic state. Gold complexes in aqueous solutions may exist as either aurous (+1) or the auric (+3) oxidation states. The stability of gold (I) and gold (III) complexes decreases as the electronegativity of the ligand atom [73]. These ligands can be ions, e.g. Cl^-, CN^-, SCN^- or uncharged molecules, e.g. NH_3, H_2O, $(NH_2)_2CS$. The stability constant β_n of a complex formed from a cation, M^{z+} and n moles of ligands, L^{y-} is defined in the Equation 43 and 44.

$$M^{z+} + nL^{y-} \leftrightarrow ML_n^{z-ny} \tag{39}$$

$$\beta_n = \frac{[ML_n^{z-ny}]}{[M^{z+}][L^{y-}]^n} \tag{40}$$

Where [i] represents the activity of species in dilute solutions.

Gold dissolves in oxidizing solutions containing leachants such as cyanide, halides, thiourea, thiosulfate and thiocyanate. Gold gives the aurocyanide complex $Au(CN)_2^-$ when it is leached by cyanide [74]. The rate of anodic dissolution of the gold in ligands subject to this study compared to cyanide is as follows: $CN^- > SCN^- > S_2O_3^{2-}$.

During dissolution of gold in cyanide solution, as a first step, oxygen is reduced and hydrogen peroxide is formed as an intermediate product and hydrogen peroxide becomes the oxidizing agent in the second step. The overall chemical reactions are presented in the following reactions.

$$2Au + 4CN^{-} + O_2 + 2H_2O \rightarrow 2Au(CN)_2^{-} + H_2O_2 + 2OH^{-} \quad (41)$$

$$2Au + 4CN^{-} + H_2O_2 \rightarrow 2Au(CN)_2^{-} + 2OH^{-} \quad (42)$$

The summation of Equations 41 and 42 is presented in the following equation [75],

$$4Au + 8CN^{-} + O_2 + 2H_2O \rightarrow 4Au(CN)_2^{-} + 4OH^{-} \quad (43)$$

This equation is called the Elsner's equation.

Gold dissolution also involves an anodic reaction of gold oxidation and a cathodic reaction of oxygen reduction [76].

The overall anodic reaction is presented in Equation 44 [77].

$$Au(CN)_2^{-} + e^{-} \leftrightarrow Au + 2CN^{-} \quad (44)$$

Cathodic reduction reactions of oxygen are shown in Equation 45.

$$O_2 + 2H_2O + 2e^{-} \leftrightarrow 2OH^{-} + H_2O_2 \quad (45)$$

Hydrogen peroxide formed in Equation 45 decomposes to H_2O and O_2, as shown in Equation 46.

$$H_2O_2 \leftrightarrow H_2O + ½ O_2 \quad (46)$$

The stability of the gold (I) with its common ligands is as follows $CN^{-}>S_2O_3^{2-}>SCN^{-}$ [78]. Stability constants for gold(I) and gold(III) with different ligands are shown in Table 3 [73]. As shown in the table gold cyanide complexes are more stable compared to the both thiocyanate and thiosulfate.

Ligand	**Au(I), β_2**	**Au(III), β_3**
CN^{-}	2×10^{38}	10^{56}
SCN^{-}	1.3×10^{17}	10^{42}
$S_2O_3^{2-}$	5×10^{28}	-

Table 3. Stability Constants for Selected Gold Complexes

Silver cyanidation involves the following reactions [79],

$$2Ag + 4CN^{-} + O_2 + 2H_2O \leftrightarrow 2Ag(CN)^{-} + 2OH + H_2O_2 \quad (47)$$

$$2Ag + 4CN^{-} + H_2O_2 \leftrightarrow 2Ag(CN)_2^{-} + 2OH^{-} \quad (48)$$

$$4Ag + 8CN^{-} + O_2 + 2H_2O \leftrightarrow 4Ag(CN)_2^{-} + 4OH^{-} \quad (49)$$

Gold dissolves in alkaline solutions of thiosulfate and forms two gold complexes, $Au(S_2O_3)^{-}$ and $Au(S_2O_3)_2^{3-}$ [80]. The dissolution of gold in thiosulfate solutions is presented in the following reaction [81],

$$4\ Au + 8\ S_2O_3^{2-} + O_2 + 2H_2O \leftrightarrow 4[Au(S_2O_3)_2]^{3-} + 4\ OH^{-} \quad (50)$$

Silver dissolution reaction in thiosulfate solutions is presented in Equation 51,

$$4Ag + 8S_2O_3^{2-} + O_2 \rightarrow 4\ [Ag(S_2O_3)_2]^{3-} + 4OH^{-} \quad (51)$$

Equilibrium constants for silver reaction with cyanide, sulfide, sulfate and thiosulfate are presented in Table 4 [82]. The magnitude of the equilibrium constants shows some of the silver-thiosulfate reactions occur faster than silver-cyanide reactions.

Reactions	**$\log_{10}$ K**
$Ag^+ + 2CN^- \leftrightarrow Ag(CN)_2^-$	20
$Ag^+ + 2CN^- \leftrightarrow Ag(CN)_3^{2-}$	20.3
$Ag^+ + 4CN^- \leftrightarrow Ag(CN)_4^{3-}$	20.8
$Ag^+ + SO_3^{2-} \leftrightarrow Ag(SO_3)^-$	5.6
$Ag^+ + 3SO_3^{2-} \quad Ag(SO_3)_2^{3-}$	7.8
$Ag^+ + 3SO_3^{2-} \leftrightarrow Ag(SO_3)_3^{5-}$	9.0
$Ag^+ \; S_2O_3^{2-} \leftrightarrow Ag(S_2O_3)^-$	8.82
$Ag^+ + 2S_2O_3^{2-} \leftrightarrow Ag(S_2O_3)_2^{3-}$	12.6
$Ag^+ + 3S_2O_3^{2-} \leftrightarrow Ag(S_2O_3)_3^{5-}$	12.8
$2Ag^+ + 4S_2O_3^{2-} \leftrightarrow Ag_2(S_2O_3)_4^{6-}$	26.3
$3Ag^+ + 5S_2O_3^{2-} \leftrightarrow Ag_3(S_2O_3)_5^{7-}$	39.8
$6Ag^+ + 8S_2O_3^{2-} \leftrightarrow Ag_6(S_2O_3)_8^{10-}$	78.6
$Ag^+ + SCN^- \leftrightarrow Ag(SCN)$	4.8
$Ag^+ + 2SCN^- \leftrightarrow Ag(SCN)^{2-}$	8.2
$Ag^+ + 3SCN^- \leftrightarrow Ag(SCN)_3^{2-}$	9.5
$Ag^+ + 4SCN^- \leftrightarrow Ag(SCN)_4^{2-}$	9.7

Table 4. Equilibrium Constants for Silver Reactions

Silver is generally co-existed with gold in the ore and leached during gold cyanidation. Silver may have both positive and negative effects on gold cyanidation kinetics depending on the mineralogy of the ore [83].

2.8 KINETICS OF GOLD AND SILVER DISSOLUTION IN CYANIDE

The gold and silver dissolution process is electrochemical in nature [84]. The mechanism of the dissolution in an alkaline cyanide solution is a heterogeneous reaction at the solid liquid interface. The leach reactions occur by the diffusion of the cyanide ions and the dissolved oxygen through the liquid film on the surface of solid particles. According to this theory the rate of cyanidation is presented by the following equation [4] :

$$Rate\ = \frac{2\ A\ D_{CN^-}\ D_{O_2}\ [CN^-][O_2]}{\delta\{D_{CN^-}[CN^-]+4\ D_{O_2}[O_2]\}} \tag{52}$$

Where,

$[CN^-]$ and $[O_2]$: Concentrations (in moles/ml) of cyanide and dissolved oxygen

$D_{CN^-}\ and\ D_{O_2}$:Diffusion coefficients of cyanide and dissolved oxygen

A : Surface area of the metal in contact with aqueous phase, in cm^2

δ : Thickness of the boundary layer

The cyanide leaching process is affected by several factors including particle size, cyanide concentration, oxygen concentration, solution temperature, pH, slurry density, speed of agitation factors. Low dissolved oxygen in leach solutions will retard the rate of gold and silver dissolution. When oxygen diffuse directly into the micropores of ore particles, in that case oxygen molecules will have retardation effect on gold cyanide complex diffusing out of these pores. Any micropore filled with gas or liquid prior to cyanidation will have retardation effect on the gold dissolution rate.

Cyanide concentrations in leach solutions are much higher than the dissolved oxygen since the oxygen saturation limit is 7 ppm. Because of this concentration difference between them, cyanide solution diffusivity to the rock pores is faster than oxygen. In conclusion, cyanide is not the rate limiting factor during the leaching process whereas dissolved oxygen becomes rate limiting factor during the diffusive transport and chemical reaction steps of leaching process [38].

2.7.1 EFFECT OF PARTICLE SIZE

The rate of dissolution depends on the surface area of the metal exposed to leaching with the lixiviant. The liberation size of the ore should be reached by a size reduction processes to have higher recovery rates of the leaching reactions. There is a linear relationship between the gold particle sizes ranging between 10 to 100 µm and the dissolution time required [85]. Another study reported similar results as in Figure 11 which show the gold dissolution amounts at the end of the 24-hour leach time at room temperature.

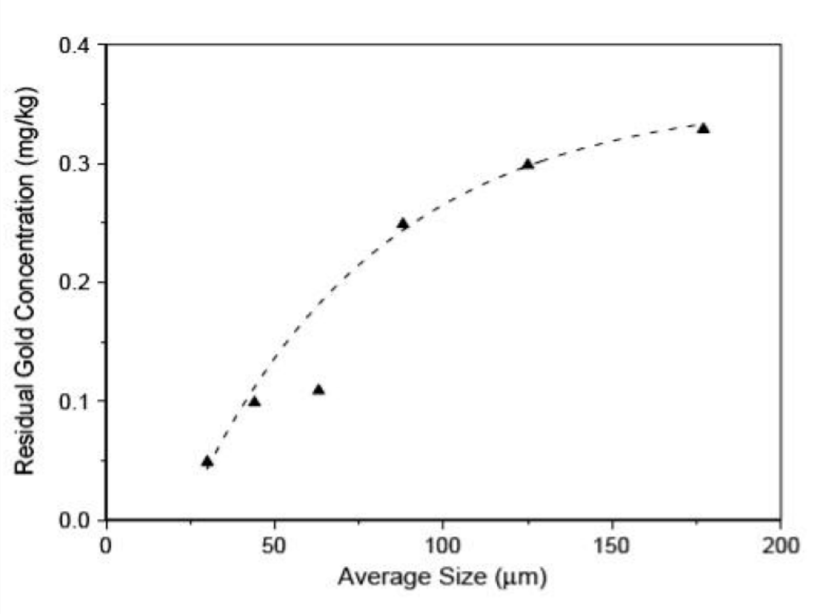


Figure 11. Particle Size Effect on Residual Gold Concentration During Cyanide Leaching [86]

On the other hand, the rate of gold dissolution may decrease with decreased particle size by liberation of other cyanide consuming elements, e.g. Fe, As, in the ore.

2.7.2 CYANIDE CONCENTRATION

Two moles of cyanide are consumed for one mole of gold dissolved during the dissolution of gold in cyanide solution. This is also shown by Elsner's equation. The rate of gold dissolution is one-half the rate of cyanide consumption [4] :

$$\text{Rate of gold dissolution} = \tfrac{1}{2}\, d(CN^-) / dt \qquad (53)$$

Gold extraction increases with increasing cyanide concentration [31]. Gold leaching will increase with increased cyanide concentration in air-saturated solutions when the cyanide concentration is below the critical concentration value 0.1 % by weight of the solution (1000 ppm). Above this molar concentration, increasing the level of cyanide in leach solutions has no positive effect on gold recoveries [74]. Also, the excess cyanide will cause an increase in cyanide consumption due to formation of cyano complexes from impurities [87].

2.7.3 OXYGEN CONCENTRATION

Oxygen is the second most important reagent in leaching of gold bearing ores by cyanide. The concentration of gold determines the concentration of the cathodic reduction of oxygen.

As shown in Equation 41, two (2) moles of gold requires one (1) mole of oxygen gas (O_2). The amount of oxygen dissolved in dilute solution mainly depends on temperature, oxygen partial pressure conditions and agitation speed.

While higher concentrations of oxygen and cyanide increases gold leaching rates, as indicated in the previous section, after a certain cyanide concentration level metal leaching rates will not increase. According to the mixed potential theory, oxidation of gold and reduction of oxygen does take place at the same rate. On the basis of this theory, the optimum concentration of $[CN^-] / [O_2]$ has been estimated to be 6 for the maximum rate of gold dissolution in cyanide solutions [88].

According to another study [89], the optimum ratio of $[CN^-]$ / $[O_2]$ is found to be between 4.6 – 6.3.

The diffusion of oxygen to the gold surface is another dissolution rate controlling parameter during leaching [90]. All particles in slurry should be suspended by sufficient agitation to ensure mass transfer of dissolved O_2 and CN^- ions to be fast enough for the surface reactions during the leaching process. A reaction mechanism to describe rate of gold leaching is presented below [91].

$$d[Au(I)]/dt = k\,[CN]^{-0.5}\,[O_2]^{0.5} \qquad (54)$$

This leach rate equation is one-half order in the concentrations of cyanide and oxygen and does take into consideration the transport steps of leaching.

3. EXPERIMENTAL STUDY

Detailed description of materials, test equipment and experimental procedures are given in the following sections.

3.1 ANALYTICAL EQUIPMENT

3.1.1 ATOMIC ABSORPTION SPECTROMETER (AAS)

A Varian Spectra 55B model atomic absorption spectrometer was used for the leach and wash solution gold, silver and copper content analyses. Equipment specifications are summarized in Table 5 and a photo of the AAS is provided in Figure 12.

Beam	True double
Display	Built-in LCD screen
Gas controllers	Manual control
Ignition control	Push button, automatic flame off
Burner-Atomizer	Changeable, premix universal atomizer
Au detection limit (micro gram/Liter)	9
Wave length range (nm)	185 – 425
UV Radiation intensity	185 – 900
Scattering (nm/mm)	3.2 – 2.4
Replicates	1 – 10
Working curve	Blank and 5 standards, 1 algorithm

Table 5. Varian Spectra 55B AAS Specifications

Figure 12. Varian Spectra 55B AAS

3.1.2 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

An Agilent 1100 series high performance liquid chromatography with ultraviolet (UV) absorbance detection was used to separate and quantify sulfur species in leach solutions. This system pumps the leach solution samples in the solvent through an adsorption column under high pressure. HPLC can separate and identify any sulfur species of interest that can be dissolved in a solvent in trace concentrations as low as parts per trillion. Substance detection in solution was accomplished by using UV detection. This detection method is based on quantifying the amount of UV light of known wavelength absorbed by the compounds of interest in leach solutions. The height of the peaks on the y-axis of the chromatography plot shows the milli absorbance unit (mAU) representing how much of the UV light was absorbed by each sulfur species and the x-axis shows the retention time. HPLC identifies each compound by its retention time, which depends on the interaction between the stationary phase, type of solvents used and type of compounds that are analyzed. HPLC system used throughout the experiments is presented in Figure 13.

The UV absorbance detection system was used to detect separated compound peaks after they elute from the column. The information coming from the UV detector was sent to the computer screen and different sulfur species could be seen in the chromatogram.

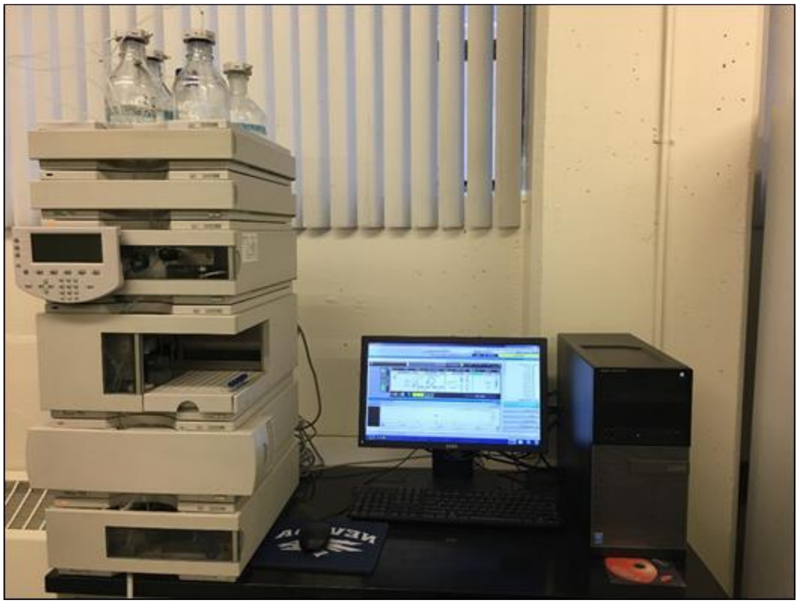


Figure 13. Agilent 1100 Series HPLC System

The time the solute needs to be transported with the mobile phase until it gets eluted is defined as void time (t_0), the net retention time (t) is where the solute is in stationary phase and the sum of net retention and void time ($t + t_0$) is the retention time (t_R). Figure 14 shows the retention and void time in a chromatography plot.

Initially, standards with known amount of each sulfur species was used for the calibration of the chromatograph. Following the completion of calibration, filtrated leach solutions were injected to the HPLC to analyze the concentration of the sulfur species of interest.

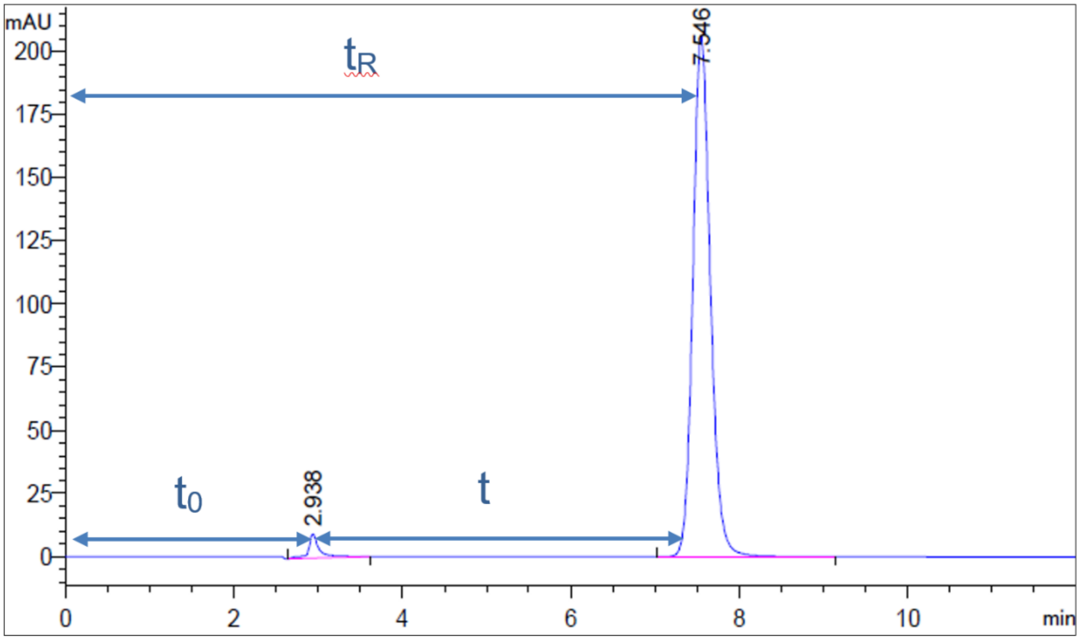


Figure 14. Net Retention and Void Time

3.1.3 INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

Perkin Elmer Optima 8300 DV ICP-OES system was used to analyze full chemical composition of the flotation tailings head assays. The analysis principle of ICP-OES is as follows, initially the sample solutions are fed into a spray chamber inside the equipment. From this chamber, each sample solution is carried by argon gas into a torch with a temperature of 10,000 ^{o}C. The protons emitted from the ionized gaseous mixture by the heat of the torch are collected on the equipment's lens. A photodetector used to convert the wavelength of the atoms on the lens to an electrical signal which than converts it to elemental information by processing in a computer. The amount of element reported by the computer is proportional to its energy intensity emitted at a particular wavelength. The general layout of an ICP-OES equipment is shown in Figure 15.

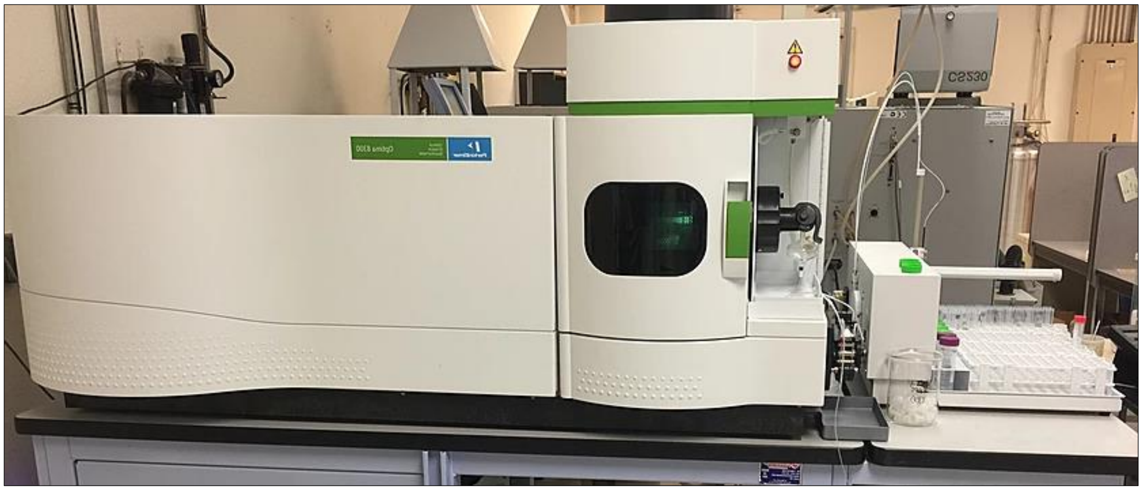


Figure 15. Perkin Elmer Optima 8300 DV ICP-OES

3.1.4 CYANIDE ANALYZER

The analytical CNSolution 3202 Cyanide Analyzer was used to measure the available cyanide in precious metal leach solutions by employing USEPA OIA-1677 method. CNSolution 3202 provided the applicability of gas-diffusion amperometry type analysis which avoided interferences from copper and metallic sulfides. Cyanide analyzing system is shown in Figure 16.

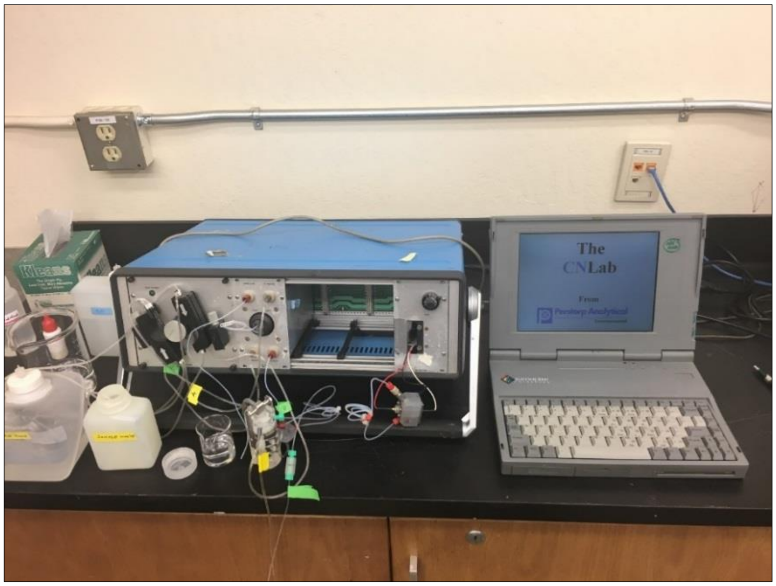


Figure 16. CNSOLUTION 3202 Cyanide Analyzer

The detector response for each sample was displayed on the computer screen as a peak in real time during the leach solution analysis.

General specifications of the system are shown in Table 6.

Operating principle	Gas diffusion amperometry
Measurement	Amperometric detection – silver electrode
Calibration	4 point calibration
Measurement	± 5% T 50 ppm
Analysis time	3 minutes
Reagents required	DI water, NaOH, HCl solutions and CN^- standards
Data export	To PC via ethernet

Table 6. CN Analyzer System Specifications

3.1.5 LECO CARBON AND SULFUR ANALYZER

The Leco CS series carbon/sulfur analyzer by combustion was used for analytical quantification of the sulfur and carbon content of the head and tailing samples.

Figure 17. Leco CS Series

For the sulfur content analysis, solid samples were put in a ceramic crucible and weighed. Following this, iron was added as an accelerator to speed up the chemical reactions on the next step. The sample crucible was placed in the induction furnace of the analyzer and melted in a pure oxygen atmosphere. During the pyrometallurgical process, sulfur content of the samples reacts with oxygen (O_2) forming sulfur dioxide (SO_2) and carbon content reacts with oxygen (O_2) forming carbon monoxide (CO) and carbon dioxide (CO_2). Both sulfur and carbon detection throughout this process was completed by the infrared cells. The gases produced during the combustion process were passed through a dust filter and purified by a moisture absorber. Initially, sulfur dioxide absorbed as a gas on the filter was quantified. Following this step both carbon monoxide and sulfur dioxide was oxidized to sulfur trioxide (SO_3). And sulfur trioxide was removed by cellulose wool and carbon content was quantified.

3.2 MATERIALS

3.2.1 SODIUM TRITHIONATE

There was no commercially available trithionate to be used for HPLC standard preparation. In order to define the trithionate retention time on the ion chromatography results, high concentrate (70 – 80% pure) trithionate standards were prepared at the research lab. Trithionate standard preparation procedure steps are presented below [92],

1. 62 g of sodium thiosulfate 5-hydrate was dissolved in 50 ml of D.I. water by stirring the solution mechanically.
2. Prepared solution was cooled down to 0-10 ^{o}C.
3. While stirring and keeping the thiosulfate solution temperature between 0 - 10 ^{o}C, 52 ml of 30% hydrogen peroxide was added by drops to the thiosulfate solution.
4. Sodium sulfate precipitates by the Reaction 55 between thiosulfate and hydrogen peroxide,

$$2\ Na_2S_2O_3 + 4\ H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4\ H_2O \qquad (55)$$

5. The precipitated sodium sulfate removed by filtering solution through a Buchner funnel.

6. The hydrated product is obtained by evaporating the filtrate.

3.2.2 SODIUM TETRATHIONATE DIHYDRATE

Sodium tetrathionate dihydrate was used for high performance liquid chromatography (HPLC) calibrations and to artificially spike bottle roll solution tetrathionate concentrations. In order to prepare 1000 ppm tetrathionate stock solution, 0.1366 g $NaO_3SS_2SO_3Na{\cdot}2H_2O$, was added to 100 ml volumetric flask filled with DI water. 0.1, 1, 5 ml of this stock solution was added to 100 ml flask filled with DI water to prepare 1, 10, 50 ppm standard solutions, respectively. The calculation steps for the tetrathionate stock solution are shown in Table 7.

Sodium tetrathionate	**$Na_2S_4O_6.2H_2O$**	
Sample	0.1366	g
Molecular weight	306.27	g
Mole	0.00045	mol
$S_4O_6^{2-}$ molecular weight	224.2564	g
$S_4O_6^{2-}$ sample weight	0.1000	g
Solution volume	100	ml
$S_4O_6^{2-}$	1000	ppm

Table 7. Sodium Tetrathionate Dihydrate Stock Solution Calculations

The specifications of the sodium tetrathionate dihydrate is shown in Table 8.

Manufacturer	Sigma Aldrich
Product number	101576034
CAS Number	13721-29-4
Assay	≥98%
Ca	≤500 mg/kg
Cd	≤50 mg/kg
Co	≤50 mg/kg
Cu	≤50 mg/kg
Fe	≤50 mg/kg
K	≤100 mg/kg
Ni	≤50 mg/kg
Pb	≤50 mg/kg
Zn	≤50 mg/kg

Table 8. Sodium Tetrathionate Dihydrate Specifications

3.2.3 SODIUM THIOSULFATE PENTAHYDRATE

Sodium thiosulfate pentahydrate was used to calibrate the HPLC. In order to prepare 1000 ppm thiosulfate stock solution, 0.2212 g $Na_2S_2O_3 \cdot 5H_2O$, was added to 100 ml volumetric flask filled with DI water. 0.1, 1, 5 ml of this stock solution was added to 100 ml flask filled with DI water to prepare 1, 10, 50 ppm standard solutions, respectively. The calculation steps for the thiosulfate stock solution are shown in Table 9.

Sodium thiosulfate	**$Na_2S_2O_3.5H_2O$**	
Sample	0.2212	g
Molecular weight	248.11	g
Mole	0.0009	mol
S_2O_3 molecular	112.1282	g
S_2O_3 sample weight	0.1000	g
Solution volume	100	ml
S_2O_3	1000	ppm

Table 9. Sodium Thiosulfate Pentahydrate Stock Solution Calculations

The specifications of the sodium thiosulfate pentahydrate are shown in Table 10.

Manufacturer	Macron
Product number	8100-04
CAS Number	1010217-7
Assay	≥99%, HPLC grade
Insoluble Matter	<= 0.005 %
Nitrogen Compounds (as N)	<= 0.002 %
Sulfate and Sulfite (as SO_4)	<= 0.1 %

Table 10. Sodium Thiosulfate Pentahydrate

3.2.4 SODIUM THIOCYANATE

Sodium thiocyanate was used to prepare HPLC standards. 1000 ppm thiocyanate stock solution was prepared by adding 0.1396 g NaSCN to 100 ml volumetric flask filled with DI water. 0.1, 1, 5 ml of this stock solution was added to 100 ml flask filled with DI water in order to prepare 1, 10, 50 ppm standard solutions, respectively. The calculation steps for the thiocyanate stock solution are shown in Table 11.

Sodium thiocyanate	**NaSCN**	
Sample	0.1396	g
Molecular weight	81.07	g
Mole	0.00172	mol
SCN^- molecular weight	58.0824	g
SCN^- sample weight	0.1000	g
Solution volume	100	ml
SCN^-	1000	ppm

Table 11. Sodium Thiocyanate Stock Solution Calculations

The specifications of the sodium thiocyanate are shown in Table 12.

Manufacturer	VWR
Product number	0861-500G
Assay	≥99.9%
CAS Number	540-72-7
Heavy metals (as	0.0001%
Iron	0.00001%

Table 12. Sodium Thiocyanate Specifications

3.2.5 SODIUM PERCHLORATE MONO HYDRATE

Sodium perchlorate was used as an eluent for the HPLC analysis. The calculation steps for 0.2 M sodium perchlorate solution preparation are shown in Table 13.

Sodium perchlorate	**$NaClO_4.H_2O$**	
Sample added	24.5000	g
Density	2.4994	g/cm^3
Sample volume	9.8024	ml
Molecular weight	122.4400	g
Solvent added	990.2	ml
Sample Molarity	0.20010	M

Table 13. Sodium Perchlorate Solution Calculations

The specifications of the sodium perchlorate are shown in Table 14.

Manufacturer	Fischer scientific
Product number	S4900-500
CAS Number	7791-07-3
Assay	≥98%
Insoluble Matter	0.005%
Chloride (Cl)	0.003%
Sulfate (SO_4)	0.002%
Calcium (Ca)	0.02%
Heavy Metals (as Pb)	5 ppm
Potassium (K)	0.05%

Table 14. Sodium Perchlorate Specifications

3.2.6 SODIUM SULFITE

Sodium sulfite was used during the bottle roll experiments. 10,000 ppm sulfite stock solution was prepared by adding 0.1573 g Na_2SO_3 to 100 ml volumetric flask filled with DI water. 3, 6 and 9 ml of this stock solution was added to 300 ml bottle roll solutions in order to increase the solution's initial sulfite ion content to 100, 200 and 300 ppm, respectively. The calculation steps for the sodium sulfite stock solution and sodium sulfite chemical specifications are shown in Table 15 and Table 16, respectively.

Sodium sulfite	**Na_2SO_3**	
Sample	1.5743	g
Molecular weight	126.04	g/mol
Mole	0.0125	mol
SO_3^{2-} molecular weight	80.07	g/mol
SO_3^{2-}sample weight	1.0000	g
Solution volume	100	ml
SO_3^{2-}	10,000	ppm

Table 15. Sodium Sulfite Solution Calculations

Manufacturer	EMD
Product number	LCSX0785
CAS Number	7757837
Assay	≥98%
Insoluble Matter	Max 0.005%
Titrable free base	Max 0.03 mea/g
Chloride (Cl)	Max 0.02%
Heavy Metals (as Pb)	Max 0.001%
Iron (Fe)	Max 0.001%

Table 16. Sodium Sulfite Specifications

3.2.7 POTASSIUM CYANIDE

1000 ppm cyanide stock solution was prepared by adding 0.2502 g KCN to 100 ml volumetric flask filled with DI water. 0.1, 0.3, 1 and 2 ml of this stock solution was added to 100 ml flask filled with DI water in order to prepare 1, 3, 10 and 20 ppm standard solutions to be used for cyanide analyzer calibrations. The calculation steps for cyanide stock solution are shown in Table 17.

Potassium Cyanide	**KCN**	
Sample	0.2502	g
Molecular weight	65.12	g
Mole	0.00384	mol
CN^- molecular weight	26.02	g
CN^- sample weight	0.1000	g
Solution volume	100	ml
CN^-	1,000	ppm

Table 17. Potassium Cyanide Stock Solution Calculations

The specifications of the potassium cyanide are shown in Table 18.

Manufacturer	Sigma-Aldrich	Lithium (Icp)	≤ 5 mg/kg
Product number	60178-100G	Manganese (Icp)	≤ 5 mg/kg
CAS Number	151-50-8	Molybdenum (Icp)	≤ 5 mg/kg
Assay	≥98%	Sodium (Icp)	≤ 5000 mg/kg
Aluminium (Icp)	≤ 5 mg/kg	Nickel (Icp)	≤ 5 mg/kg
Bismuth (Icp)	≤ 5 mg/kg	Strontium (Icp)	≤ 5 mg/kg
Calcium (Icp)	≤ 50 mg/kg	Zinc (Icp)	≤ 5 mg/kg
Cadmium (Icp)	≤ 5 mg/kg	Arsenic (Mhs-Aas)	≤ 0.1 mg/kg
Cobalt (Icp)	≤ 5 mg/kg	Total Sulfur as SO_4 (Icp)	≤ 100 mg/kg
Chromium (Icp)	≤ 5 mg/kg	Chloride (Cl)	≤ 200 mg/kg
Copper (Icp)	≤ 5 mg/kg	Sulfide (S)	≤ 5 mg/kg

Table 18. Potassium Cyanide Specifications

3.2.8 CUPROUS CYANIDE

Cuprous cyanide was used to prepare AAS standards. 10% copper standard stock solution was prepared by adding 14.1 g CuCN to 100 ml volumetric flask filled with DI water. 5, 10, 20 ml of this stock solution was added to 100 ml flask filled with DI water in order to prepare 0.5, 1 and 2% standard solutions, respectively. The calculation steps for the copper standard stock solution are shown in Table 19.

Cuprous cyanide	**CuCN**	
Sample	14.1	g CuCN
Molecular weight	89.5634	g CuCN
Mole	0.157	mol
Cu sample weight	10.004	g
Solution volume	100	ml
CuCN	10.004	%

Table 19. Cuprous Cyanide Solution Calculations

The specifications of the cuprous cyanide are shown in Table 20.

Manufacturer	Sigma-Aldrich
Product number	208-883-6
CAS Number	544-92-3

Table 20. Cuprous Cyanide Specifications

3.2.9 SILVER CYANIDE

Silver cyanide was used to prepare AAS standards. 100 ppm silver standard stock solution was prepared by adding 0.0124 g AgCN to 100 ml volumetric flask filled with DI water. 0.1, 1, 5, 10, 50 ml of this stock solution was added to 100 ml flask filled with DI water in order to prepare 0.1, 1, 5, 10, 50 ppm standard solutions, respectively. The calculation steps for the silver standard stock solution are shown in Table 21.

Silver cyanide	**AgCN**	
Sample	0.0124	g
Molecular	133.89	g
Mole	0.000093	mol
Ag sample	0.0100	g
Solution	100	ml
AgCN	100	ppm

Table 21. Silver Cyanide Solution Calculations

The specifications of the silver cyanide are shown in Table 22.

Manufacturer	Sigma Aldrich
Product number	184535
CAS Number	506-64-9

Table 22. Silver Cyanide Specifications

3.2.10 AUROUS CYANIDE

Aurous cyanide was used to prepare AAS standards. 100 ppm gold standard stock solution was prepared by adding 0.0113 g to 100 ml volumetric filled with DI water. 0.1, 1, 5, 10 ml of this stock solution was added to 100 ml flask filled with DI water in order to prepare 0.1, 1, 5, 10 ppm standard solutions, respectively. The calculation steps for the gold standard stock solution are shown in Table 23.

Aurous cyanide	**AuCN**	
Sample	0.0113	g
Molecular weight	222.984	g
Mole	0.000051	mol
Au sample weight	0.0100	g
Solution volume	100	ml
AuCN	100	ppm

Table 23. Gold Cyanide Solution Calculations

Table 24 shows the specifications of the aurous cyanide.

Manufacturer	Sigma Aldrich
Product number	298115
CAS Number	13967-50-5

Table 24. Aurous Cyanide Specifications

3.2.11 HYDROCHLORIC ACID

Hydrochloric acid was used to convert available cyanide in sampled leach solutions to HCN gas during the quantification of the available cyanide. A 0.2 M HCl solution was prepared for each cyanide analyzing process. The calculation steps for 0.2 M acid solution are shown in Table 25.

Hydrochloric acid	**HCl**	
Sample	16.2	ml
Density	1.2	g/ml
Molecular weight HCl	37	g
Sample Molarity	12	M
Weight %	37%	
HCl	7.1928	g
H^+ molecular weight	1	g
Cl molecular weight	35.45	g
H^+ sample weight	0.2029	g
H^+ mol	0.2029	
Solution volume	1000	ml
H^-	0.203	M

Table 25. Hydrochloric Acid Solution Calculations

The specifications of the hydrochloric acid are shown in Table 26.

Hydrochloric acid	**HCl**
Titration with NaOH	36.5 - 38.0
Residue on Ignition	< 5 ppm
Arsenic (As)	< 0.01
Bromide	< 0.005 %
Iron (Fe)	< 0.2 ppm
Free Chlorine	< 1 ppm
Heavy Metals	< 1 ppm
Ammonium	< 3 ppm
Sulfite (ppm)	< 1 ppm
Sulfate	< 1 ppm

Table 26. Hydrochloric Acid Specifications

3.2.12 SODIUM HYDROXIDE

Sodium hydroxide (NaOH) is highly soluble in water and dissociates in water solutions to form sodium cations and hydroxide anions as shown on Equation 56 [93]. Sodium hydroxide solubility in water is 109 g/100 ml at 20°C [94].

$$NaOH_{(s)} + H_2O_{(l)} \rightarrow Na_{(aq)} + OH^{-}_{(aq)} + H_2O_{(l)} \quad (56)$$

Sodium hydroxide was used as the base to increase the pH of the standard solution preparation for the AAS standards, and to convert generated HCN gas to free cyanide during available cyanide analysis. Calculation steps to prepare 0.2 M NaOH solution are shown in Table 27.

Sodium Hydroxide	**NaOH**	
Sample	8	g
Molecular weight	39.997	g
Mol	0.20002	mol
OH^- molecular weight	17.008	g
OH^- sample weight	3.4019	g
Solution volume	1000	ml
Molarity OH^-	0.2000	M

Table 27. Sodium Hydroxide Solution Calculations

Table 28 summarizes the properties of the sodium hydroxide used throughout the experiments [95].

Manufacturer	JT Baker	Copper (%)	0.001
Product number	3722	Potassium (%)	0.01
CAS Number	1310-73-2	Nitrogen Compounds	3
Assay (%)	98.0	Phosphate (ppm)	2
Na_2CO_3 (%)	0.4	Sulfate (ppm)	5
Calcium (%)	0.005	Iron (ppm)	3
Chloride (%)	0.001	Mercury (ppm)	0.1
Heavy Metals (%)	0.001	Nickel (ppm)	5

Table 28. Sodium Hydroxide Composition

3.2.13 CALCIUM OXIDE

Calcium oxide was used to increase the pH of the solutions during the bottle roll experiments. Calcium oxide solubility in water is 0.125 g/100 ml of water at 20°C [94] . Calcium oxide forms calcium hydroxide in water by the following reaction [96].

$$CaO_{(s)} + H_2O_{(l)} \leftrightarrow Ca(OH)_{2(aq)} \quad (57)$$

The calcium oxide used for the experiments was the typical pH modifier that the mining companies generally use; the specific material used was from a sample taken from bulk facility outside Carlin, NV. Table 29 summarizes the properties of the calcium oxide used throughout the experiments [97].

Manufacturer	Graymont
Product number	-
CAS Number	1305-78-8
Assay (%)	90 Min
MgO (%)	1.3
R_2O_3 (%)	0.7
SiO_2 (%)	0.5 Max
SO_3 (%)	1.3 Max
CO_2 (%)	2.5

Table 29. Calcium Oxide Composition

3.2.14 SODIUM CYANIDE

Sodium cyanide (NaCN) is an inorganic compound that has high reactivity with metals. Sodium cyanide fully dissociates in water and forms metal cation and free cyanide ions.

Sodium cyanide was used as leaching agent to recover gold and silver from the slurries during the bottle roll experiments. The calculation steps for sodium cyanide dosage for the bottle roll experiments are presented in Table 30.

Sodium	**NaCN**	
Sample	0.1500	g
Molecular	49.01	g/mol
Mole	0.0031	mol
Solution	300	ml
NaCN	500	ppm

Table 30. Sodium Cyanide Dosage Calculations

Table 31 summarizes the properties of the sodium cyanide used throughout the experiments [98].

Manufacturer	Sigma Aldrich	Sodium	0.5 Max.
Product number	380970	Sodium	0.3 Max.
CAS Number	143-33-9	Sodium	0.05 Max.
Assay (%)	97 Min	Water (%)	0.2 Max.
Sodium Formate (%)	0.5 Max.	Insoluble	0.05 Max.

Table 31. Sodium Cyanide Composition

3.2.15 DIONIZED (DI) WATER

High quality dionized water with a conductivity of about 18.2 megohm-cm was used for all experiments and chemical standards.

Initially recycled mine water was decided to be used for the bottle roll slurries to better simulate the actual plant conditions. Since the recycled water had high content of sulfur species and considering their varying interactions based in temperature, time and light, DI water was used for slurry preparations.

DI water and recycled mine water ion chromatography analyses are shown in the following figures and tables for the comparison purposes.

Signal 1: DAD1 A, **Sig=215,4** Ref=280,10

Peak #	**RetTime [min]**	**Type**	**Width [min]**	**Area [mAU*s]**	**Height [mAU]**	**Area %**
1	2.84	BV	0.089	915.6	146.1	4.1
2	3.59	VV	0.098	7,605.7	1200.3	33.9
3	3.85	VB	0.104	8,573.0	1254.5	38.2
4	5.53	BB	0.142	14.5	1.6	0.1
5	7.48	BB	0.210	3,684.5	271.7	16.4
6	9.42	BB	0.272	1,668.3	95.3	7.4
Totals:				22,461.6	2969.4	

Table 32. Mine Water IC Analysis

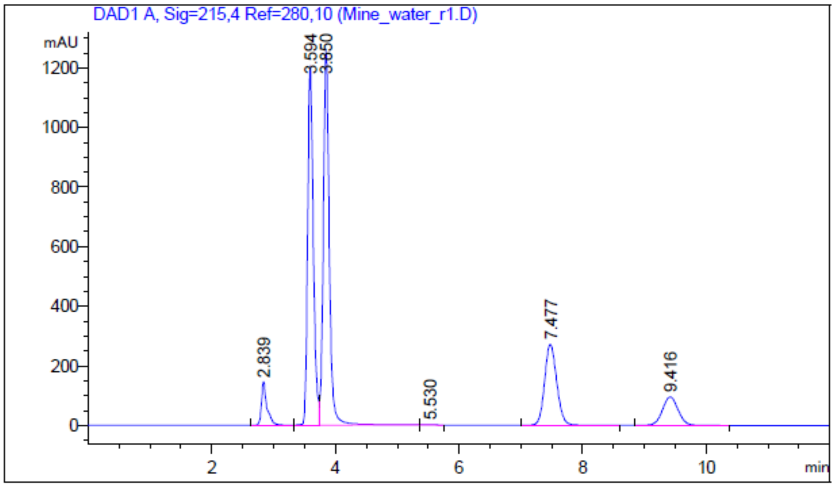


Figure 18. Mine Water IC Analysis

Signal 1: DAD1 A, **Sig=215,4** Ref=280,10

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.878	BV	0.1252	16.1	1.69	40.4
2	2.965	VB	0.1672	23.8	1.83	59.6
Totals :				39.9	3.53	

Table 33. DI water IC analysis

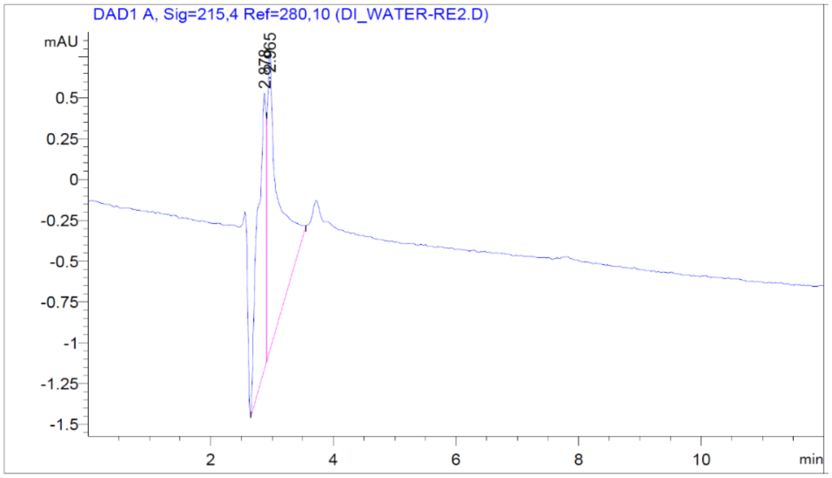


Figure 19. DI Water IC Analysis

3.3 FLOTATION TAILING SAMPLES

In August 2016, 10 gallons of flotation tailings slurry was received by the staff of Mining and Metallurgical Engineering Department of University of Nevada, Reno (UNR). The samples were characterized in the accompanying documentation as carbon in leach (CIL) feed flotation tailings. Dried flotation tailings samples were leached by bottle roll method under different conditions. Fire assay, Leco, inductively coupled plasma (ICP) and cyanide shake tests were conducted on dry head assays and leached flotation tailings. Additionally, leach solutions were analyzed for their metal and sulfur species content, and WAD cyanide concentrations.

Figure 20. Flotation Tailings Samples

The total gold (AuFA) and cyanide soluble gold (AuCN) contents of the flotation tailings samples were 0.1953 and 0.0444 troy ounce per short ton, respectively. The cyanide shake tests showed that only 23 % of the total gold content was amenable to cyanide leaching for the flotation tailing samples.

The amount of sulfide sulfur (SS), sulfate sulfur (SRO) and total sulfur content (STOT) of the samples were %10.98, %1.91 and %12.89, respectively. Flotation tailings samples were primarily selected for the experimental test work because of their high sulfide sulfur content. Additionally, relatively high gold content of flotation tailing samples provided better observation of recovery changes during the experiments. The abbreviations for the chemical analyses made on the head samples are given in Table 34. Chemical composition of the flotation tailings samples is presented in Table 35.

Abbreviation	**Unit**	**Definition**
Ag	toz/st	Silver
Al	ppm	Aluminum
As	ppm	Arsenic
AuCN	toz/st	Cyanide Soluble
AuFA	toz/st	Total Gold
Ba	ppm	Barium
Bi	ppm	Bismuth
C. Or.	%	Organic Carbon
Ca	%	Calcium
C. Ino.	%	Inorganic Carbon
Cd	ppm	Cadmium
Co	ppm	Cobalt
Cu	%	Copper
Fe	%	Iron
Hg	ppm	Mercury
Li	ppm	Lithium
Mg	ppm	Magnesium
Mn	ppm	Manganese
Mo	ppm	Molybdenum
Na	%	Sodium
Ni	ppm	Nickel
Pb	ppm	Lead
P	%	Phosphorus
Sb	ppm	Antimony
Se	ppm	Selenium
Sn	ppm	Tin
Sr	ppm	Strontium
SRO	%	Sulfate Sulfur
SS	%	Sulfide Sulfur
STOT	%	Total Sulfur
Te	ppm	Tellurium
Ti	ppm	Titanium
Tl	ppm	Thallium
V	ppm	Vanadium
Zn	ppm	Zinc

Table 34. Chemical Analysis Table Abbreviations

Ag	**Al**	**As**	**AuCN**	**AuFA**	**Ba**
3.0220	1.34	1620	0.0444	0.1953	358
Bi	**Ca**	**Cd**	**Co**	**C Or.**	**C. Ino.**
46	2.44	55	100	0.44	0.46
C	**Cu**	**Fe**	**Hg**	**Li**	**Mg**
0.9	2.02	19.30	0.04	9	7.69
Mn	**Mo**	**Na**	**Ni**	**Pb**	**P**
995	233	0.14	363	935	0.06
Sb	**Se**	**Sn**	**Sr**	**SRO**	**SS**
49	57	0.01	24	1.91	10.98
STOT	**Ti**	**Te**	**Tl**	**V**	**Zn**
12.89	728	63	3	<1	3240

Table 35. Flotation Tailings Samples Chemical Composition

3.4 EXPERIMENTAL PROCEDURES

Test work of this study included particle size analysis, bottle roll experiments, cyanide species analysis, ion chromatography with ultraviolet absorbance detection, atomic absorption analysis, Leco sulfur analysis, cyanide shake tests, inductively coupled plasma mass spectrometry and fire assay.

Flotation tailings slurry that was received from the mine site was initially decanted to lower the liquid content of the samples. Following this, high solid content (≈70%) slurry was dried in the oven at 30 ^{o}C to avoid any sulfur oxidation. The dried solids were than used as the feed for the bottle roll tests.

Bottle roll slurries with 50% solid by weight were leached for 12 hours at initial pH values between 10.6 to 11.6. The flotation tailings slurry pH values varied between 6.95 and 7.30. Multiple trials were conducted to determine the amount of calcium oxide required to increase the bottle roll initial pH values to approximately 11. At the end of these trials, 1.5 g CaO per 300 g solid samples (10 lb/st) was found as the necessary amount to be added to the bottle rolls to reach the desired slurry pH values at the beginning of the experiments.

In order to investigate the effects of the sulfite salts on cyanide consumptions and metal recoveries, different amounts of sulfite solutions were added to the bottle roll slurries. Bottle roll experiments were conducted by adjusting sulfite dosages in the slurry initially to 0, 100, 200, 300 ppm under different cyanide concentrations.

Except for the control experiments, bottle roll slurry solutions' tetrathionate content initially spiked to 300 ppm to investigate tetrathionate ion effect on metal recoveries and cyanide consumptions. Experiments were conducted with initial target cyanide levels varying between 250 to 1000 ppm in order to define an optimum cyanide-sulfite level point. Each experiment was duplicated to measure the consistencies of the analytical measurements. Table 36 summarizes bottle roll experimental conditions. Amounts of each reagent added to the bottle roll experiments are presented in Appendix A.

Exp.#	**Solids (g)**	**Water (g)**	**% solids**	**Leach (hrs)**	**NaCN lb/st ore**	**Initial target NaCN (ppm)**	**Initial target $S_4O_6^{2-}$ (ppm)**	**Initial target SO_3^{2-} (ppm)**
BR1	300	300	50%	12	0.50	250	0	0
BR7	300	300	50%	12	1.00	500	0	0
BR8	300	300	50%	12	1.00	500	300	0
BR9	300	300	50%	12	1.00	500	300	100
BR10	300	300	50%	12	1.00	500	300	200
BR11	300	300	50%	12	1.00	500	300	300
BR27	300	300	50%	12	1.00	500	0	0
BR28	300	300	50%	12	1.00	500	300	0
BR29	300	300	50%	12	1.00	500	300	100
BR30	300	300	50%	12	1.00	500	300	200
BR31	300	300	50%	12	1.00	500	300	300
BR42	300	300	50%	12	1.50	750	0	0
BR18	300	300	50%	12	1.50	750	300	0
BR19	300	300	50%	12	1.50	750	300	100
BR20	300	300	50%	12	1.50	750	300	200
BR21	300	300	50%	12	1.50	750	300	300
BR22	300	300	50%	12	1.50	750	0	0
BR23	300	300	50%	12	1.50	750	300	0
BR24	300	300	50%	12	1.50	750	300	100
BR25	300	300	50%	12	1.50	750	300	200
BR26	300	300	50%	12	1.50	750	300	300
BR45	300	300	50%	12	2.00	1000	0	0
BR33	300	300	50%	12	2.00	1000	300	0
BR34	300	300	50%	12	2.00	1000	300	100
BR35	300	300	50%	12	2.00	1000	300	200
BR36	300	300	50%	12	2.00	1000	300	300
BR37	300	300	50%	12	2.00	1000	0	0
BR38	300	300	50%	12	2.00	1000	300	0
BR39	300	300	50%	12	2.00	1000	300	100
BR40	300	300	50%	12	2.00	1000	300	200
BR41	300	300	50%	12	2.00	1000	300	300

Table 36. Experimental Scope

Bottle weight, bottle + solid, bottle + solid + water weights were measured and recorded at each step of material addition to the bottles. The weights values for each experiment is presented on Appendix A. Initially, slurry in the bottles was mixed for 5 minutes and the natural pH of the slurry was recorded. Following this, calcium oxide, required amount of tetrathionate and sulfite solution were added to the bottle roll slurries and bottles were rolled additional 15 minutes. At the end of this 15-minute period, bottle roll pH values were measured and recorded again. Following this, required amounts of cyanide were added to the bottles and were left to be mixed on the rollers for a 12-hour period. At the end of the 12 hours, slurry pH values were measured again and recorded. Bottle roll slurries were sampled, centrifuged, and injection filtered. Clear leach solutions were analyzed for their cyanide content, sulfur species concentrations and metal contents. The remaining slurry in the bottle rolls was filtered. Wash solutions were sampled and further analyzed for their metal content. Filtrates were dried at 30 ^{o}C, sampled and their metal content were analyzed by fire assay.

Figure 21 presents the experimental sequence followed for the bottle roll experiments and analytical measurements. Experimental procedures followed throughout the expriments are presented in the rest of the section 3.

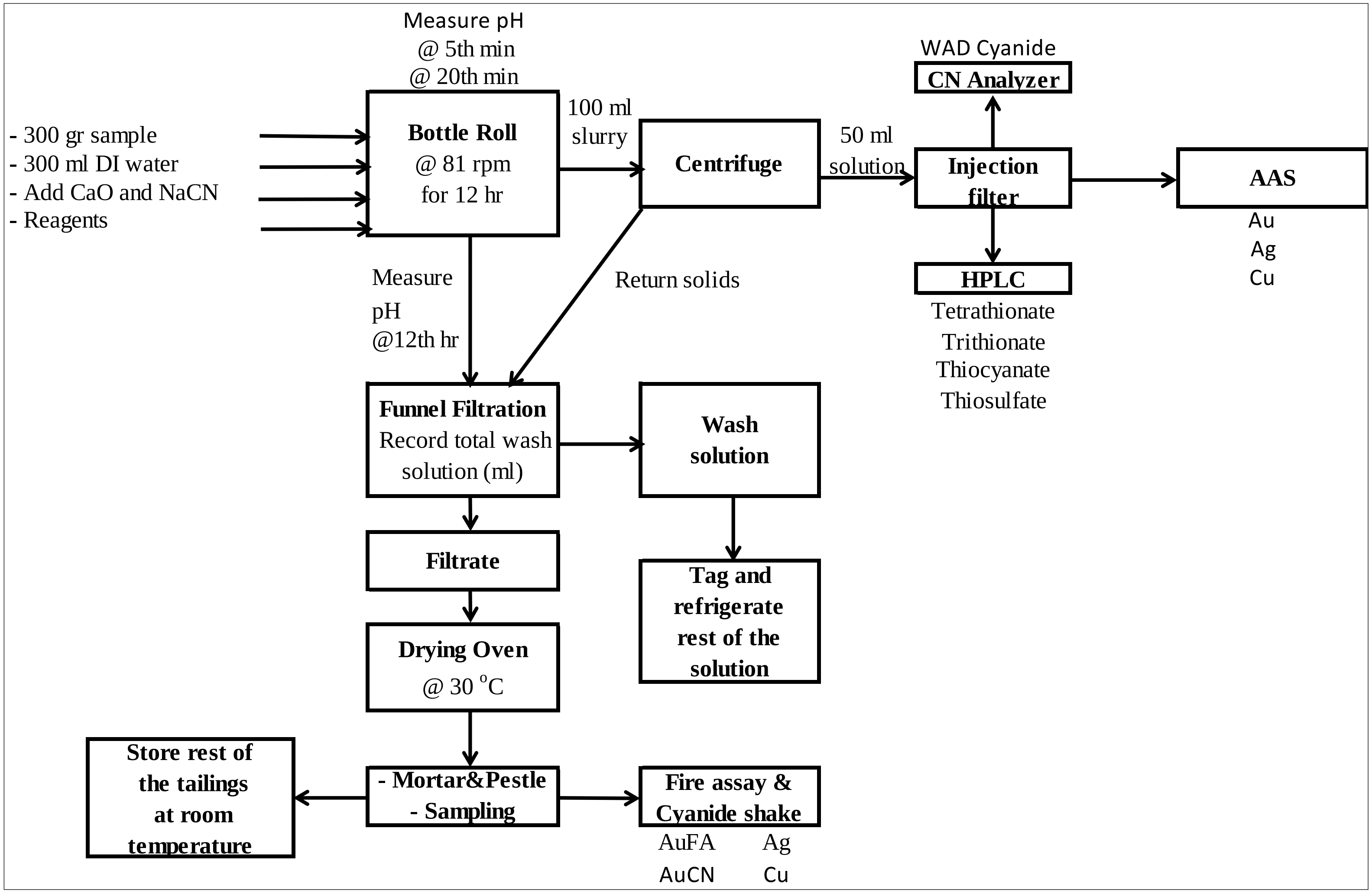


Figure 21. Sample Collection and Analysis Diagram

3.4.1 SAMPLE SPLIT

Sample split procedure was applied to maintain homogeneity of the samples and avoid the nugget effect during sample size reduction. The sampling procedure applied is summarized below [99],

1. Entire sample was passed four times over the top of the riffle splitter for blending purposes.

2. As the sample was passed over the riffle, samples were collected in two catch pans at the bottom of the riffle.

3. The splitter and pans were cleaned at the end of the sampling procedure using compressed air.

As shown in Figure 22 split was combined and split again after the first split to ensure the material blending.

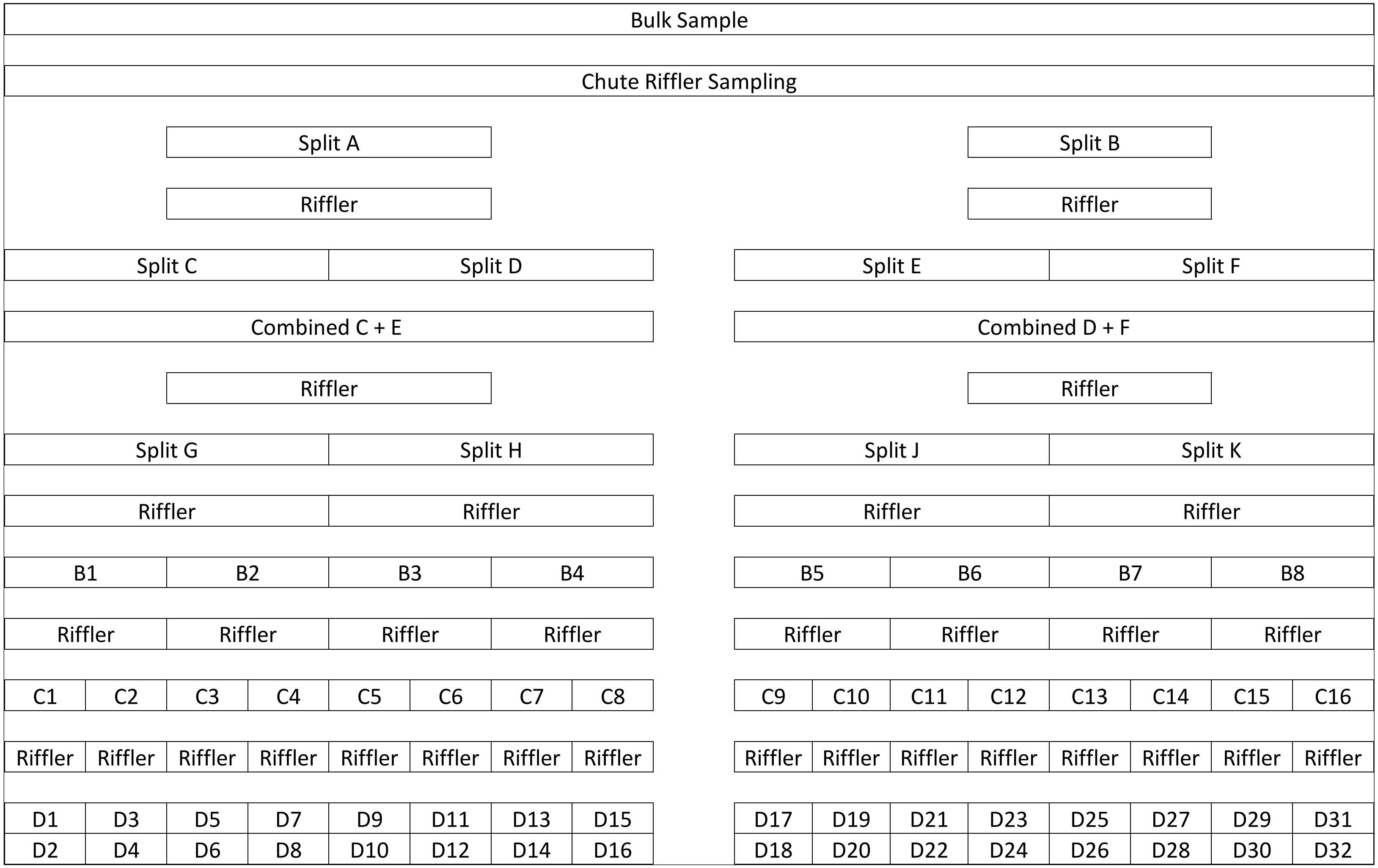


Figure 22. Sampling Procedure

3.4.2 FILTRATION

At the end of the bottle roll experiments, leach slurries were filtered with a porcelain funnel filtration and flask unit. Two products, the filtrate and wash solution were obtained at the end of the filtration process and both of them were analyzed for their total gold, cyanide soluble gold, silver and copper content. The filtration procedure is summarized below,

1. Two layers of filter paper were placed over the porcelain funnel base.
2. The filter paper was wetted with a minimum amount of water to improve the filter seal.
3. Vacuum hose was connected to the flask suction channel and the vacuum valve was opened.
4. Slurry was poured slowly into the funnel.
5. Filtration continued until a very small amount of solution was coming out the drain valve.
6. The vacuum hose was disconnected and its value was closed.
7. The filter paper with the remaining filtrate on it were removed.

3.4.3 DRYING

Following the filtration, solid samples were dried in a lab oven. Drying procedure was as follows,

1. Batch oven temperature controller was adjusted 30 ^{o}C.

2. At the end of the drying period samples were removed from the oven, stirred and checked for any water condensation under a watch glass.
3. Any sample with moisture content was returned to the oven for further drying.

3.4.4 PARTICLE SIZE ANALYSIS

The procedure for the size analysis of samples was as follows:

1. Dry weights of the samples were recorded.

2. The sample was placed in a 500 ml beaker to make a 20% solid by weight slurry.

3. Small quantities of the slurry were placed onto the sieve and sprayed with wash water (Wet screening).

4. Periodically +200 mesh material was unloaded to a separate pan. No more than 50 g of material was loaded on the screen at any time to protect the screen from overloading.

5. +200 and -200 mesh materials were dried in an oven at 30 ^{o}C for 24 hours.

6. The dried +200 mesh material was used as feed material for dry screening tests.

7. +200 mesh material was loaded into a series of screens and placed on the rotap for 10 minutes. 200 mesh screen and two pans (above and below the screen) were placed into the rotap for size analysis purposes.

8. Sieves were unloaded and the weights of the retained samples were recorded.

9. Oversize and undersize materials were combined separately.

10. Weights of dry screening material were reported.

Figure 23 shows summary of the particle size analysis procedure.

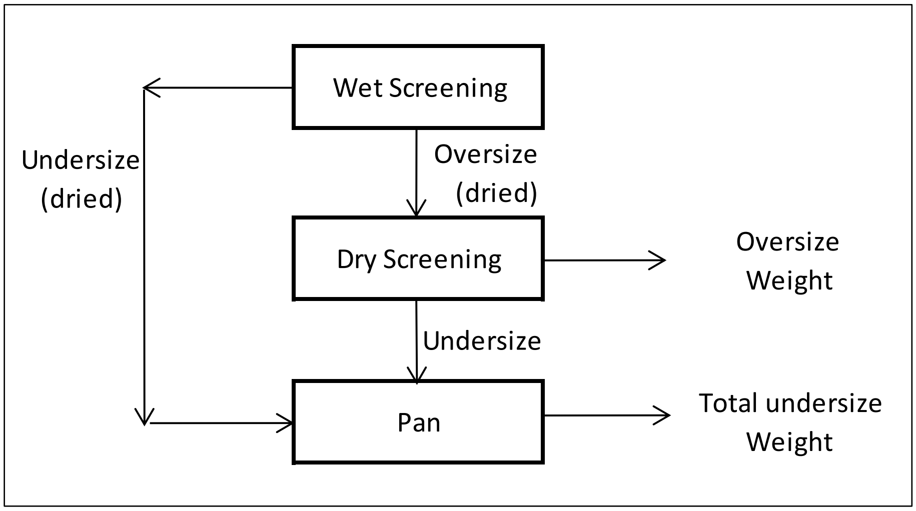


Figure 23. Particle Size Analysis Procedure

3.4.5 BOTTLE ROLL TESTS

Cyanide bottle roll experiments were performed in order to leach gold from flotation tailings under different conditions. A total of forty-eight bottle roll leach tests were conducted on the composite samples of the flotation tailings samples.

The experimental procedure is summarized below,

1. 300 g flotation tailings sample was placed into a clean 0.7 gallon bottle.

2. Roller rpm was adjusted to 83 rpm (8 on the controller)

3. 300 mL DI water was placed into the bottle and the formed slurry was rolled for 5 min, than the pH was checked.

4. After 5 min of initial conditioning lime was added (sulfite, tetrathionate or any additional reagent was added as indicated for the test procedure) bottles were rolled for another 15 min and pH was checked. The amounts of reagents added and the value of the pH was recorded.

5. At the end of the 15-min. sodium cyanide (NaCN) was added to the solution. Bottle was placed on a standard roller to agitate the slurry for 12 hrs.

6. After 12 hours, the roller was stopped and slurry samples were taken, as follows:

A) 100 ml of sample was transferred to a centrifuge test tube.

B) Slurry sample was centrifuged, decanted and clear solution was syringe filtered. Reject pulp was returned to the bottle.

C) The clear sample solution was analyzed for pH, sulfur species, WAD cyanide, Au, Ag and Cu content.

7. At the end of each test, dry tailings were filtered through a funnel, washed and weighed. The dried tailings were fire assayed in duplicate for Au, Ag and Cu content. All solid sample were stored in the refrigerator, until assayed.

8. A sample from filtration solutions was taken for AAS analysis and rest of the wash solutions were stored in the refrigerator. All filtrate and wash volumes were recorded. The final wash solution was assayed for Au, Ag and Cu. Metal recovery was calculated as metal extracted via solution plus tailings assay.

3.4.6 FIRE ASSAY

The gold content of head and tailing samples was determined by the conventional fire assay method. Fire assaying procedure consists of sample preparation, fluxing and fusion, cupellation, parting and annealing [100].

Sample preparation: Received samples were split and pulverized.

Fluxing and Fusion: Samples were melted with the proper flux in a crucible at 1100°C inside the fire assaying oven. Assay fluxes were composed of litharge, borax, silica sand, sodium carbonate and wheat flour. Wheat flour acted as a reducing agent and forms metallic lead, sodium carbonate was added for de-sulfurization, borax and silica were added to modify the melting point and helps control the viscosity of the melted impurities. The amounts of sodium carbonate (Na_2CO_3), litharge (PbO), silica (SiO_2), borax ($Na_2B_4O_7$) and wheat flour added were 27%, 53.5%, 13.5%, 4.5%, 1.5%, respectively. Figure 24 shows the fire assaying oven where fluxes and samples were melted inside the crucibles.

Figure 24. Fire Assaying Ovens

After complete melting of the samples, the crucibles were removed from the furnace and the contents were poured into a mold. After solidification of all contents of the crucible, a lead button formed at the bottom of the crucible and a slag formed above it. The slag and the lead button formed were broken by hammer and separated from each other. The lead button obtained, was used for the cupellation process [101].

<u>Cupellation:</u> Lead buttons were placed into the cupels were loaded into the cupellation kiln at 950^{o}C. At his temperature lead buttons melted and lead oxide

absorbed into the cupel leaving behind a tiny doré bead containing gold and silver. After the cupellation was completed, the cupel was removed from the furnace and allowed to cool. The doré beads derived from cupellation were weighed. The hot cupels and the formed dore beads are shown in Figure 25 and Figure 26, respectively.

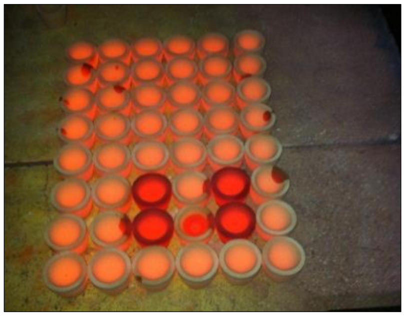


Figure 25. Removed Cupels from the Furnace

Figure 26. Doré Bead Containing Gold and Silver in Cupels

<u>Determination of the Gold and Silver Amount of the Buttons:</u> The doré was placed in a porcelain cup. Nitric acid (15% by volume) was added to the cup and heated on a hotplate. The nitric acid dissolved the silver and left a gold sponge behind. The sponge was washed with de-ionized water and left to dry. The gold sponge

was annealed and then weighed by using a microbalance [102]. The Au weight and the initial weight of the dore were used to determine Ag (opt), by difference.

Figure 27. Microbalance

3.4.7 CYANIDE ANALYZER

WAD cyanide analyses were completed by the following steps:

1. Available cyanide in sample solutions was converted to HCN under acidic conditions.
2. HCN gas was diffused across a hydrophobic membrane within the membrane separator and HCN was collected in the acceptor solution.
3. HCN converted back to CN^- in acceptor solution was carried into the flow cell of the amperometric detector. Following this, cyanide ions reacted with the silver electrode generating a current proportional to cyanide ion concentration.

4. Detector responses sent from analyzer to computer and final cyanide concentrations were calculated based on the calibration curve.

Figure 28 shows the steps for the cyanide analyzing method.

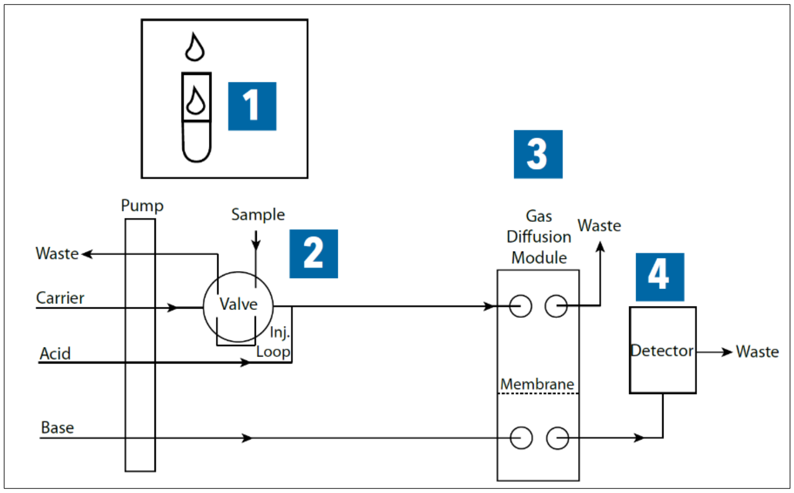


Figure 28. Cyanide Analyzer Operation Principle [103]

3.4.8 ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Atomic absorption spectroscopy (AAS) is a spectro analytical procedure for determining chemical element quantities. This is accomplished by the measurement of absorbed radiation by free atoms of the chemical elements in the gaseous state [104].

The gold, silver and copper amounts (analyte) in each leach solution sampled were assessed by the absorption spectrometry technique. A standard with known analyte content was initially measured to define a relation between the measured absorbance and analyte concentration.

Overall analysis procedure followed is summarized below,

After turning on the compressed air and acetylene cylinder valves connected to the AAS, the instrument was turned on. Following the display on instrument screen, below instrument parameters were entered for the metal analyses.

Instrument mode : Absorbance

Active lamp : 2

Active current (mA) : 4.0

Standby current (mA) : 0

D2 correction : No

Gas type : Air, acetylene

Wave length (nm) : 242.8 (Gold), 328.1 (Silver), 327.4 (Copper)

Slit : 1

Measurement parameters were set up as follows:

Next sample : 1

Batch number : 1

Pre-read delay : 10 sec

Read time : 4 sec

Replicates : 3

After setting up the spectrometer parameters, a Varian card was used to make light beam alignment and additional 45 minutes spent for the gold lamp to warm up until the readings were stable.

Once the readings were stable, the spectrometer was calibrated by using 0, 0.5, 1, 5, 10 ppm gold; 0, 1, 5, 10, 25, 50 ppm silver, % 0, 0.5, 1, 2 copper standards in 0.1% NaCN and 1% NaOH solution.

3.4.9 LEACHABLE GOLD IN PULP BY CYANIDE SHAKE TEST

A shake test was applied to analyze the ore samples' refractory nature and response to cyanidation.

Shake test experimental procedure is presented below,

1. All test tubes were numbered and labeled.
2. 15 g of pulverized samples were added to 50 mL glass test tubes.

3. 30 mL of caustic cyanide solution with the concentration of 0.5% NaCN and 0.8% NaOH was added to the test tubes
4. All the glass tubes were tapped, placed on a shaker table and agitated for 1 hour.
5. If any sample was not wetted, sample number was noted and rerun using half of the sample weight.
6. All the samples were centrifuged for 10 minutes at 3200 rpm.
7. The solution was collected from the tubes and analyzed for its gold content by AAS.

3.4.10 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

Ion chromatography (IC) method was employed to quantify the thiocyanate, thiosulfate, trithionate and tetrathionate concentrations at the end of the bottle roll leach tests. 50 µl of leach solution samples previously filtrated with 0.45 µm syringe filter was injected into the mobile phase and passed to a stationary phase in the HPLC column. Final sulfur concentrations were calculated based on calibration curves Table 37 summarizes the IC method used.

Analytical column	OMNIPAC PAX-100
Guard column	OMNIPAC PAX-100G
Sample volume	50 µl
Eluent	0.2 M $NaCl_4$
Modifier	-
Eluent flow-rate	1.2 ml/min
Detection	UV @ 215.4 and 280.10 nm
Column pressure	12.8 Mpa
Column temperature	30 ^oC
Total analysis time (min)	12
Thiosulfate retention time (min)	3.7
Thiocyanate retention time (min)	3.9
Trithionate retention time (min)	5.5
Tetrathionate retention time (min)	7.5

Table 37. IC Method

The default HPLC chromatography report contains following information, peak number, retention time (min), type of the peak, width of the peak (min), area of the peak (mAU*s), height of the peak (mAU), Area (%).

Peak separation codes are listed in the final chromatography results under the “Type” column of the peak. Each peak type was defined with a letter code.

The first letter describes the starting baseline and the second letter describes the end baseline of the peak.

"B" The peak started or stopped on the baseline.

"P" The peak started or stopped while the baseline was penetrated.

"V" The peak started or stopped with a valley drop-line.

"H" The peak started or stopped on a forced horizontal baseline.

"F" The peak started or stopped on a forced point.

"M" The peak was manually integrated.

"U" The peak was unassigned.

The third position provides the peak flags.

" " normal peak

"A" aborted

"D" distorted

"O" overrange

"U" underrange

The fourth position provides the peak type information.

" " normal peak

"S" solvent

"N" negative

"+" area sum

"T" tangent skim normal

"X" tangent skim exponential

"m" manual

"n" manual negative

"t" manual tangent skim

"x" manual exponential tangent skim

"R" recalculated solvent peak

"f" front shoulder, tangent

"b" rear shoulder, tangent

"F" front shoulder, dropline

"B" rear shoulder, dropline

“U” unassigned

The peak width is the band width in the column. The tangent peak width shown in Figure 29 is measured by extrapolating the tangents on inflection points to the baseline.

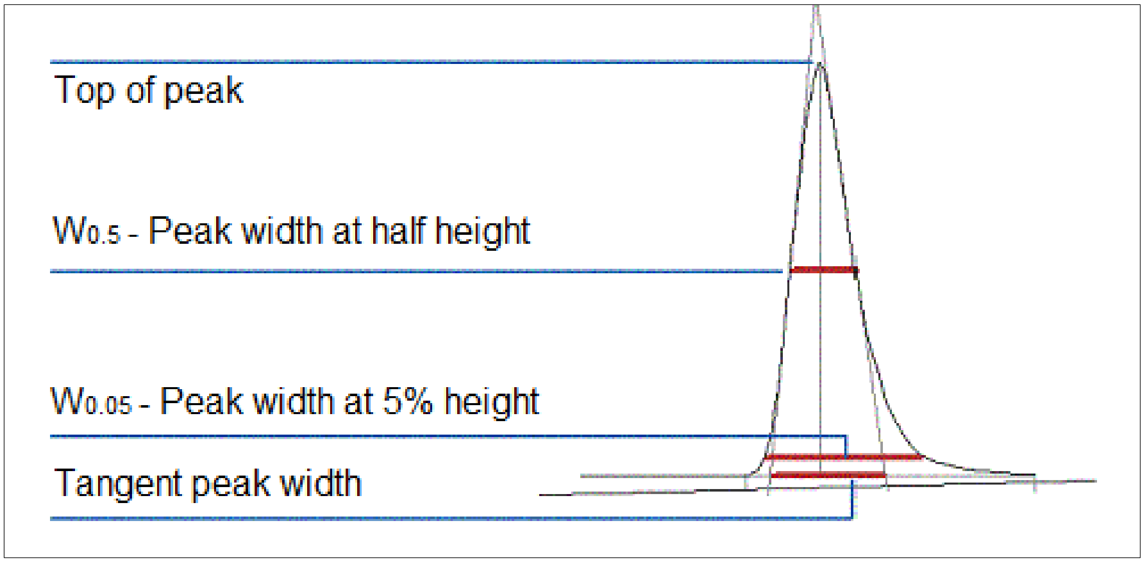


Figure 29. IC Peak Width

The peak width was calculated by the following formula,

$$Peak\ Width = 0.3\left(Inflection\ Point_{right} - Inflection\ Point_{left}\right) + 0.7\left(\frac{Area}{Height}\right)$$

The HPLC was calibrated before each leach solution analyses. Tetrathionate, thiocyanate and thiosulfate retention times, and their corresponding concentrations were determined by using HPLC grade standards..

Different concentrations of each tetrathionate, thiocyanate and thiosulfate ion was quantified individually during the calibration process. Concentration amounts of each ion were calculated by using the calibration parameters and peak areas on the graphs during leach solution analyses. The peak areas and retention times corresponding to thiosulfate, thiocyanate and tetrathionate are presented in Figures 30 – 33 and Tables 38 – 41. As shown in the figures, thiosulfate, thiocyanate and tetrathionate have 3.7, 3.9 and 7.7 minutes retention times, respectively. Figure 33 shows the chromatography of the mix of 50 ppm thiosulfate, thiocyanate and tetrathionate and Table 41. represents the corresponding peak height and areas of each ion. The first peak in each graph corresponds to the time the solute transportation with the mobile phase until it gets eluted. A full IC calibration profile is presented in Appendix C.

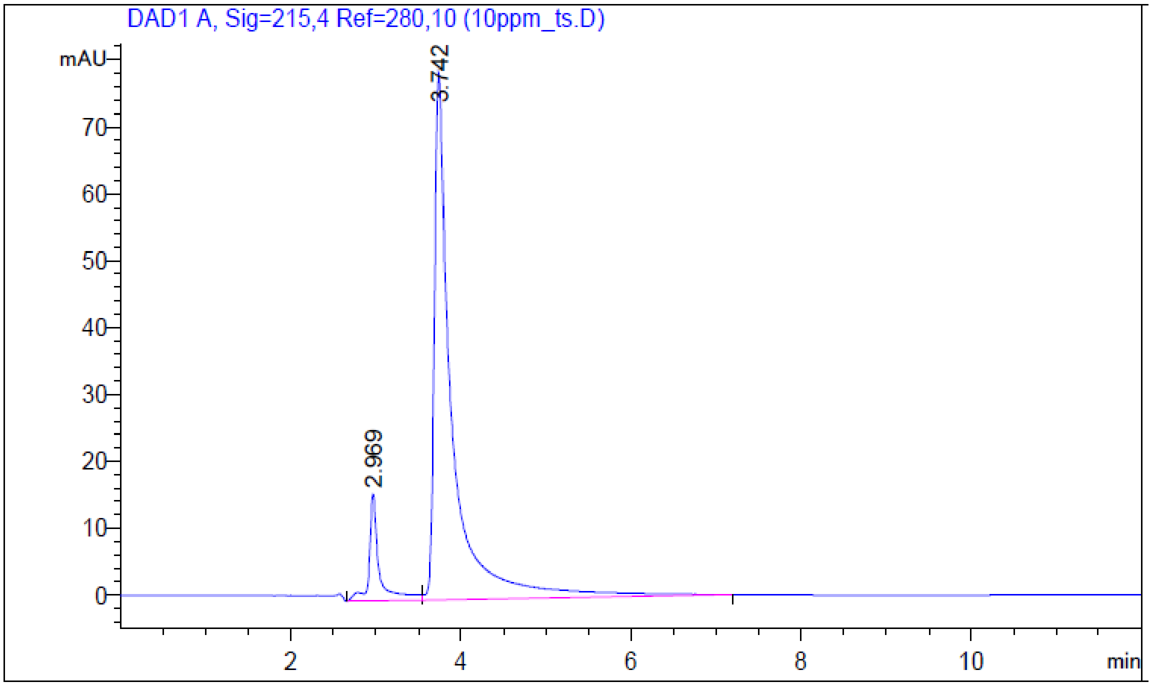


Figure 30. 10 ppm Thiosulfate IC Standard Peak

Signal 2: DAD1 B, Sig=215,4 Ref=280,10

Peak	**RetTime**	**Type**	**Width**	**Area**	**Height**	**Area**
#	**[min]**		**[min]**	**[mAU*s]**	**[mAU]**	**%**
1	2.969	BV	0.11	131.85	16.01	10.36
2	**3.742**	**VB**	**0.20**	**1,140.86**	**78.97**	**89.64**
Totals				1272.711	94.98	

Table 38. 10 ppm Thiosulfate IC Standard Report

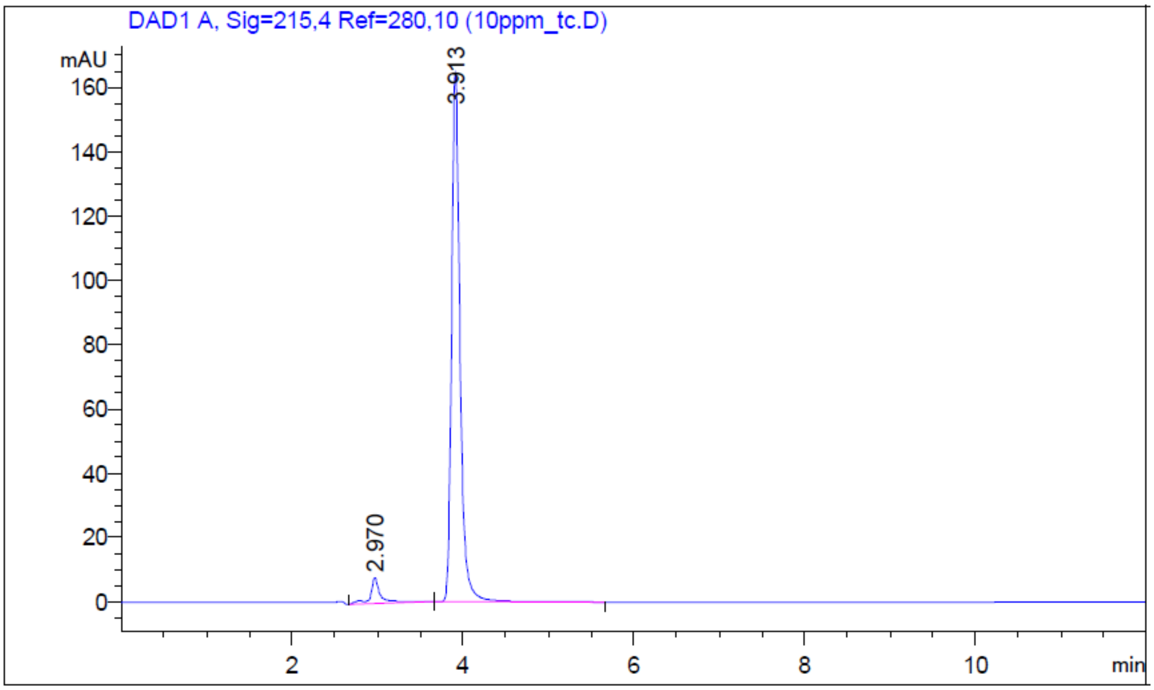


Figure 31. 10 ppm Thiocyanate IC Standard Peak

Signal 2: DAD1 B, Sig=215,4 Ref=280,10

Peak #	**RetTime [min]**	**Type**	**Width [min]**	**Area [mAU*s]**	**Height [mAU]**	**Area %**
1	2.97	BB	0.12	70.27	8.07	5.82
2	**3.913**	**BB**	**0.10**	**1,136.24**	**164.47**	**94.18**
Totals				1206.502	172.54	

Table 39. 10 ppm Thiocyanate IC Standard Report

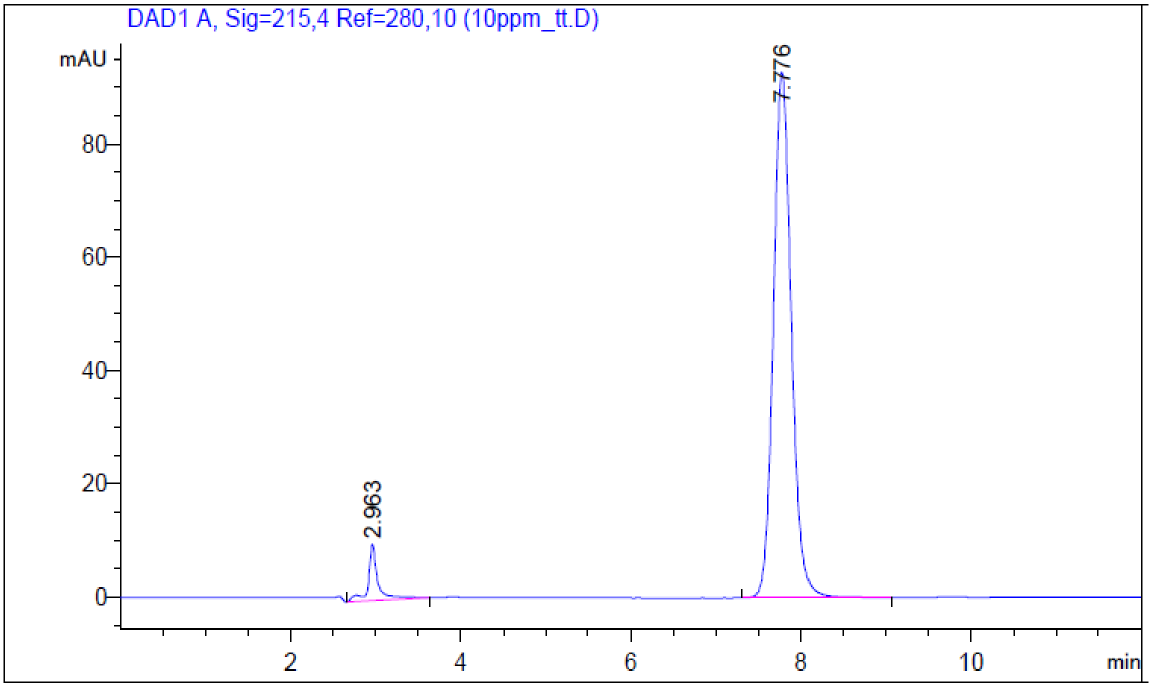


Figure 32. 10 ppm Tetrathionate IC Standard Peak

Signal 2: DAD1 B, Sig=215,4 Ref=280,10

Peak #	**RetTime [min]**	**Type**	**Width [min]**	**Area [mAU*s]**	**Height [mAU]**	**Area %**
1	2.963	BB	0.11	80.47	9.89	5.52
2	**7.776**	**BB**	**0.23**	**1,376.17**	**92.91**	**94.48**
Totals				1456.635	102.80	

Table 40. 10 ppm Tetrathionate IC Standard Report

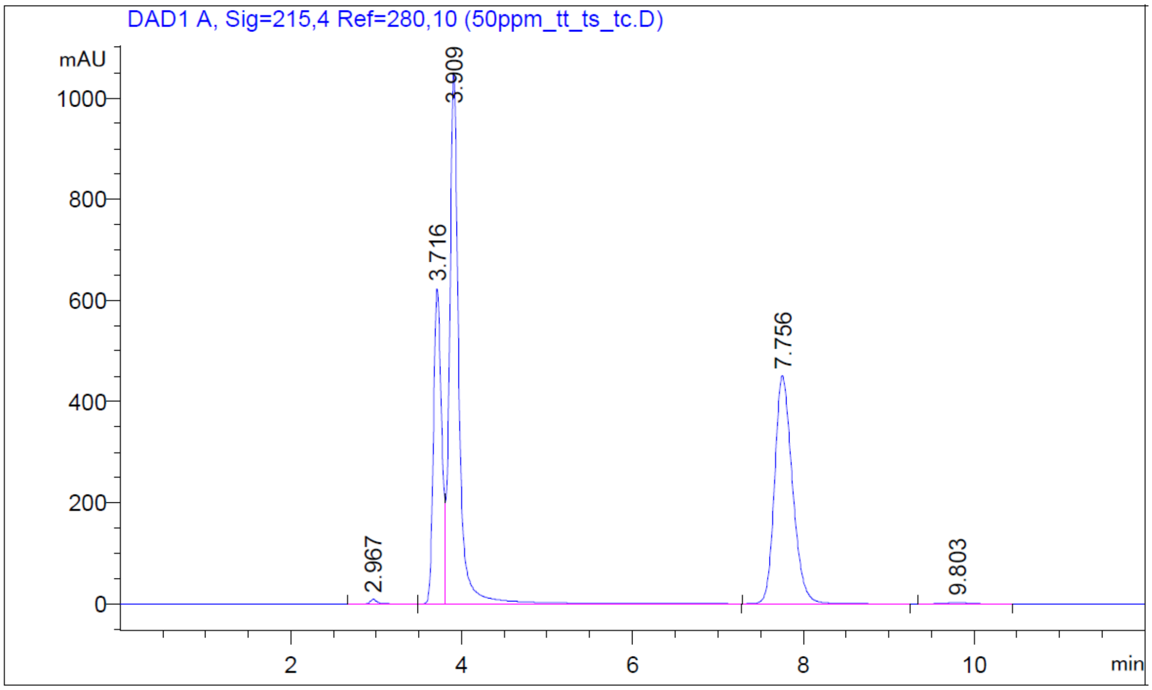


Figure 33. 50 ppm Thiosulfate, Thiocyanate and Tetrathionate IC Standard Peaks

Signal 2: DAD1 B, **Sig=192,4** Ref=280,10

Peak	**RetTime**	**Type**	**Width**	**Area**	**Height**	**Area**
#	**[min]**		**[min]**	**[mAU*s]**	**[mAU]**	**%**
1	2.967	BB	0.11	72.69	9.64	0.39
2	**3.716**	**BV**	**0.10**	**4,120.83**	**624.26**	**21.84**
3	**3.909**	**VB**	**0.11**	**8,080.85**	**1,052.55**	**42.82**
4	**7.756**	**BB**	**0.22**	**6,553.14**	**450.80**	**34.72**
5	9.803	BB	0.28	44.95	2.42	0.24
Totals				1.89E+04	2139.67	

Table 41. 50 ppm Thiosulfate, Thiocyanate and Tetrathionate IC Standard Report

The procedure that was followed to prepare trithionate standard only yields 70 to 80% pure trithionate. This standard assay grade is not precise to quantify the trithionate in leach solutions during the ion chromatography measurements. However, the trithionate standard obtained was used to confirm the trithionate peak time on the chromatographs. While the exact concentration of the ion could not be calculated, the trithionate concentration changes were reported for each bottle roll experiment by using the changes in the ion's peak areas. The resulting trithionate peak from the standard prepared in laboratory conditions is presented in Figure 34. As seen in the figure trithionate peaks at 5.58th minute.

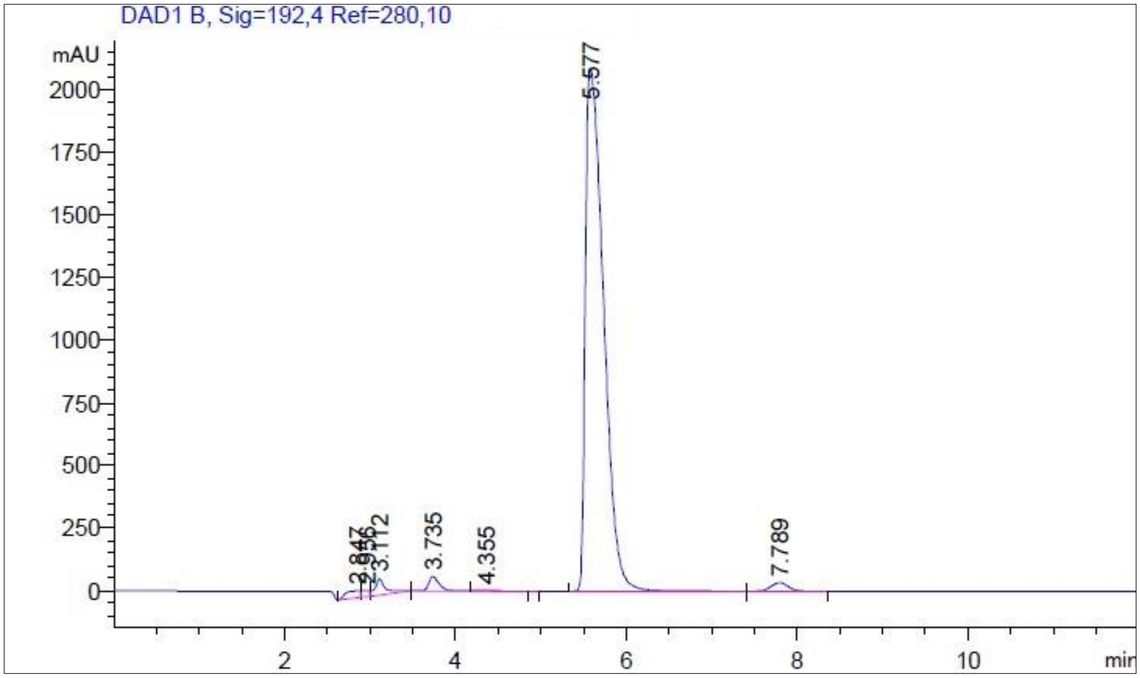


Figure 34. Trithionate Standard Ion Chromatography Results

Signal 2: DAD1 B, **Sig=192,4** Ref=280,10

Peak #	**RetTime [min]**	**Type**	**Width [min]**	**Area [mAU*s]**	**Height [mAU]**	**Area %**
1	2.847	BV	0.21	348.57	27.65	1.06
2	2.956	VV	0.10	158.02	23.67	0.48
3	3.112	VB	0.12	574.32	64.70	1.75
4	3.735	BV R	0.13	514.21	58.16	1.57
5	4.355	VB E	0.12	10.96	1.34	0.03
6	**5.577**	**BB**	**0.23**	**30,722.80**	**2,087.58**	**93.61**
7	7.789	BB	0.22	490.15	34.58	1.49
Totals			2297.7	32,818.8	2297.7	

Table 42. Trithionate Standard Ion Chromatography Results

After calibrating the HPLC, leach solutions were analyzed for their reduced sulfur species concentration. The developed IC method has resulted in definitive peaks for each of the reduced sulfur species of interest.

Figure 35 and Table 43 show the ion chromatogram of bottle roll 24. The retention times of each species in bottle roll leach solutions were in the range of ±0.1 seconds compared to the HPLC calibration standard. The peaks of each reduced sulfur species are shown in Figure 35.

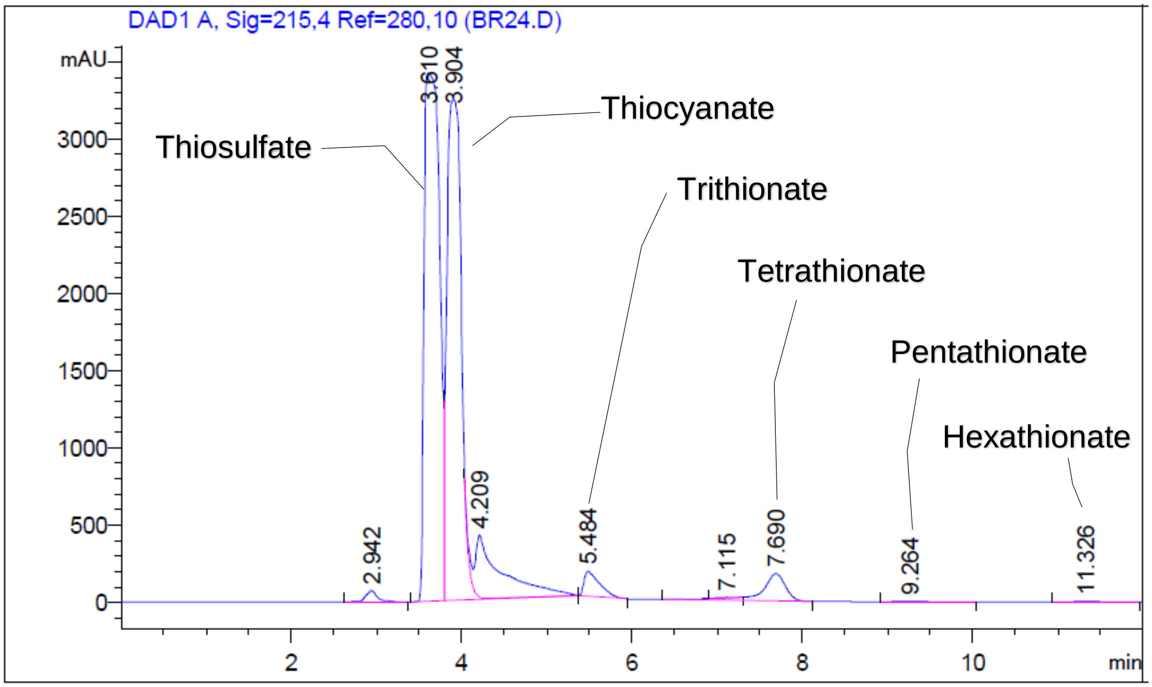


Figure 35. Bottle Roll Ion Chromatography Peaks

Signal 2: DAD1 B, **Sig=192,4** Ref=280,10

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	2.942	BB	0.15	737.69	73.97	0.76
2	**3.610**	**BV**	**0.20**	**42,630.80**	**3,423.18**	**44.01**
3	**3.904**	**VV R**	**0.19**	**38,587.20**	**3,243.20**	**39.84**
4	4.209	VB E	0.29	9,207.19	400.68	9.51
5	**5.484**	**BB**	**0.18**	**2,041.73**	**160.89**	**2.11**
6	7.115	BV E	0.22	61.01	4.41	0.06
7	**7.690**	**VB R**	**0.29**	**3,454.47**	**175.76**	**3.57**
8	9.264	BB	0.34	61.34	2.69	0.06
9	11.326	BBA	0.34	85.03	3.86	0.09
Totals				9.69E+04	7,488.63	

Table 43. Bottle Roll 24 Ion Chromatography Report

3.4.11 INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

Inductively coupled plasma spectrometry (ICP) was used for chemical analysis of flotation tailings head samples.

ICP detection limit is 10 ppb for metals and several non-metals. In this method, the solid samples were ionized with inductively coupled plasma and then by using a spectrometer the ions were separated and quantified.

US EPA Method 6010b standards were used for the ICP-OES analyses. Each solid sample was dried overnight at 30 ^{o}C and weighed prior to placing on hot plates. Solid samples analyzed were digested on hot plates at 110 ^{o}C by using 3 ml HCl, 1 ml $HCLO_4$, 2 ml HNO_3 and 2 ml HF. This procedure took nearly a day under the laboratory fume hood until the solution was dried completely. Once the samples were cooled down, additional 1 ml $HClO_4$ and 2 ml DI was added to each sample. This final solution was evaporated at 160 ^{o}C. Following this, aqua regia method was applied to the samples. The cooled sample solutions obtained from aqua regia were rinsed into graduated tubes. These digested samples were than diluted 1:5 for ICP OES analysis.

3.4.12 LECO ASSAYING

Leco assaying was used to quantify the sulfur content of flotation tailings samples. Sulfide and sulfate sulfur, total carbonaceous matter (TCM) and carbonates were assayed by Leco analysis. The Leco method consists of burning sulfur and carbon to SO_2 and CO_2, respectively, in an induction furnace and analyzing the off-gas for these species [105].

All samples submitted for either a short or long method Leco analysis were run for total carbon (carbonate + TCM) and total sulfur (sulfate sulfur + sulfide sulfur).

All samples submitted had a HCI digestion step followed by Leco burn to determine carbonate carbon by dissolving out the carbonates, i.e., calcite, dolomite and siderite, in samples and then determining the TCM remaining.

4. RESULTS AND DISCUSSION

4.1 PARTICLE SIZE ANALYSIS

Particle size analysis of the flotation tailings samples are provided in Table 44. Nearly 96% of the samples passes 200 mesh screen.

Mesh size	Sample (g)
+40	0.11
-40 +80	1.12
-80 +100	1.05
-100 +150	6.58
-150 +200	3.46
-200	286.57
Total	298.89

Table 44. Particle Size Analysis

4.2 CYANIDE ANALYSIS

As detailed in Section 3.2.7, the cyanide analyzer was calibrated with standard prepared from potassium cyanide before the leach solutions were analyzed. The WAD cyanide concentration of each leach solution were printed out from the computer screen as shown in Section 3.1.4. The results of the cyanide analyses are presented in Section 4.4.

4.3 REACTION KINETICS

The concentrations of the metals recovered, sulfur species and WAD cyanide are functions of the complex heterogeneous and homogeneous kinetics affected by both physical and chemical parameters during the bottle roll experiments. The detailed kinetics of metal and sulfur species in the leach solutions were not investigated in this study. However, the concentration change of certain sulfur and cyanide species versus time is represented on graphs to better explain the increase in metal recoveries by the sulfite salt addition to the leach slurries.

Bottle roll experiments were conducted to determine cyanide leachability of the samples. These experiments were conducted under different initial sulfite and cyanide concentrations. Each bottle roll experiment was conducted with 50% solid content by weight slurry (300 g DI water and 300 g dry sample) for 12 hours at pH values between 10.6 to 11.6 and each bottle roll experiment was duplicated to validate the experimental results. The results of the duplicate experiments are provided in Appendix B.

Bottle roll experiments were conducted as set and each set consisted of five (5) experiments. In order to compare metal recoveries and formed sulfur species concentrations based on cyanide concentration in the slurries, bottle roll experiment sets were conducted with four different initial cyanide concentrations of 250, 500, 750 and 1000 ppm.

The first bottle roll experiment of each set was conducted with only adding lime and cyanide to the slurries. This experiment was the control experiment and represented the “base-case” to all other experiments in each set.

The second experiment of each set was conducted by spiking solutions’ initial tetrathionate concentration to 300 ppm while adding the same amount of lime and cyanide as the control experiment.

The 3rd, 4th and 5th bottle roll tests in each set were run by increasing initial sulfite concentration to 100, 200 and 300 ppm, respectively while keeping the tetrathionate concentration at 300 ppm and, and adding the same cyanide and lime amounts as in the control experiments.

Bottle roll 1-6 was conducted with 250 ppm initial cyanide, 7-11 and 27-31 were conducted with 500 ppm initial cyanide, 42, 18-21 and 22-26 were conducted with 750 ppm initial cyanide, 45, 33-36 and 37-41 were conducted with 1000 ppm initial cyanide concentration.

The detailed experimental scope was presented in Table 36 of Section 3.4.

Bottle roll experiments 1-6 were not analyzed for sulfur species and metal recoveries because the selection of initial 250 ppm cyanide concentration resulted in traces of WAD cyanide (0.02 ppm) at the end of the experiments. To make sure the cyanide was not the limiting reactant throughout the experiments, lowest initial cyanide concentration was doubled to 500 ppm.

At the end of each bottle roll experiment, clear leach solutions were analyzed for their metal, sulfur species, WAD cyanide content, and the tailing samples were analyzed for their metal content.

Bottle roll experiment results are presented in Table 45.

Exp. #	Initial/ Ending pH	$S_2O_3^{2-}$ (ppm)	SCN^- (ppm)	$S_3O_6^{2-}$ (mAU*s)	$S_4O_6^{2-}$ (ppm)	WAD cyanide (ppm)	Calc. rec. Au (%)	Calc. rec. Ag (%)	Calc. rec. Cu (%)
BR1	11.61/11.46	594.4	175.9	2357.6	7.5	0.02	-	-	-
BR7	11.17/12.32	656.9	290.7	2564.10	16.2	0.06	10.2	0.30	0.09
BR8	11.07/11.60	674.2	294.3	3041.20	13.8	0.09	10.9	0.40	0.14
BR9	11.48/11.83	704.3	289.8	3410.20	16.0	0.19	11.8	0.41	0.17
BR10	11.43/12.17	725.0	283.6	3613.0	13.9	0.09	11.2	0.44	0.16
BR11	11.12/11.86	730.7	283.0	3718.0	8.6	0.16	12.0	0.44	0.16
BR27	11.52/11.07	589.7	304.0	2360.6	22.6	0.05	10.3	0.37	0.14
BR28	11.42/11.80	667.6	313.5	2778.7	22.0	0.09	9.14	0.41	0.16
BR29	11.82/12.02	657.8	309.6	2652.5	20.1	0.07	11.0	0.37	0.12
BR30	11.87/11.68	673.6	310.6	3177.4	21.8	0.21	11.4	0.48	0.22
BR31	11.77/11.86	688.7	303.0	3436.9	12.9	0.26	11.2	0.46	0.21
BR42	10/84/11.91	578.0	336.8	1121.4	30.7	11.50	13.4	0.29	0.38
BR18	11.10/11.82	600.2	294.2	1838.7	21.7	16.04	14.4	0.34	0.96
BR19	11.66/11.51	623.7	299.6	2090.6	20.6	17.29	14.1	0.37	0.70
BR20	11.25/11.73	626.2	297.1	2239.1	22.1	23.62	14.5	0.36	0.84
BR21	11.57/11.48	645.0	292.5	2406.9	20.1	25.04	14.7	0.41	0.88
BR22	10.91/10.70	598.9	312.2	1512.6	41.5	11.30	15.9	0.35	0.87
BR23	10.60/11.15	630.3	293.8	2006.3	34.3	17.02	17.0	0.42	1.23
BR24	10.98/11.17	644.8	297.4	2041.7	32.8	16.04	18.7	0.43	1.17
BR25	10.73/11.25	647.8	293.4	2068.7	34.1	23.67	16.5	0.43	1.64
BR26	10.93/11.26	656.1	291.0	3401.1	32.3	25.11	17.7	0.49	1.76
BR45	11.11/11.25	574.0	329.6	805.6	32.8	16.52	16.6	0.23	1.16
BR33	11.55/11.36	618.4	313.6	1482.9	16.1	16.47	15.7	0.42	4.16
BR34	11.33/11.37	631.6	322.0	1923.1	23.4	16.48	17.3	0.46	3.37
BR35	11.81/11.49	641.1	311.9	1976.4	23.4	16.43	17.2	0.44	4.83
BR36	11.34/11.57	660.7	308.7	2145.6	24.3	16.42	18.1	0.47	4.50
BR37	10.74/11.52	536.7	320.0	1030.7	41.0	16.55	17.2	0.30	2.01
BR38	11.64/11.89	566.7	314.3	1455.2	33.1	16.53	18.7	0.40	2.90
BR39	11.27/11.68	634.2	318.6	1643.6	33.6	16.52	18.7	0.50	3.14
BR40	11.6/11.75	637.5	321.3	2030.9	32.4	16.52	18.1	0.50	3.56
BR41	11.52/11.82	673.6	318.6	1843.6	30.5	16.49	17.3	0.64	4.35

Table 45. Experiment results

As explained in Section 2.5 higher sulfur species react with free cyanide ions in leach solutions very rapidly by the following reactions,

$CN^- + S_4O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + SCN^- + SO_4^{2-} + 2H^+$ (29)

$2CN^- + S_5O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + 2SCN^- + SO_4^{2-} + 2H^+$ (30)

$3CN^- + S_6O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + 3SCN^- + SO_4^{2-} + 2H^+$ (31)

As shown in the Equations 36 - 38, SO_3^{2-} ions cause tetrathionate, pentathionate, hexathionate ion degradation to thiosulfate and trithionate according to the following reactions [71], [72] .

$S_4O_6^{2-} + SO_3^{2-} \leftrightarrow S_2O_3^{2-} + S_3O_6^{2-}$ (36)

$S_5O_6^{2-} + 2SO_3^{2-} \leftrightarrow 2S_2O_3^{2-} + S_3O_6^{2-}$ (37)

$S_6O_6^{2-} + 3SO_3^{2-} \leftrightarrow 3S_2O_3^{2-} + S_3O_6^{2}$ (38)

Previous research shows that tetrathionate reactions with cyanide ions occur spontaneously at temperatures between 2 - 25 °C. At the same time thiosulfate reaction with cyanide will occur in the presence of cupric ions as a catalyst in the same temperature range 2 - 25 °C. The Reaction 58 of trithionate with free cyanide takes place only at temperatures between 40 – 100 °C [106].

$S_2O_3 + CN^- \leftrightarrow SCN^- + SO_3^{2-}$ (27)

$3CN^- + S_3O_6^{2-} + H_2O \leftrightarrow SO_3^{2-} + SO_4^{2-} + SCN^- + 2HCN$ (58)

Experiment results showed that by increasing the amount of sulfite ions in leach solutions, tetrathionate concentration levels decreased while trithionate levels increased due to degradation of higher polythionates as shown in reactions 36 - 38. At the same time, ending thiocyanate concentration levels in leach solutions was lower since the amount of cyanide – polythionate reactions decreased.

Another reason for trithionate concentration increase in leach solutions is due to the hydrolysis of higher polythionates, as shown in Equations 59 and 60.

$$S_5O_6^{2-} + 3\ OH^- \leftrightarrow 2.5\ S_2O_3^{2-} + 1.5\ H_2O \quad (K=10^{45}) \qquad (59)$$

$$2\ S_4O_6^{2-} + 3\ OH^- \leftrightarrow 2.5\ S_2O_3^{2-} + S_3O_6^{2-} + 1.5\ H_2O \quad (K=10^{16}) \qquad (60)$$

Figure 36, Figure 37 and Figure 38 show the tetrathionate, trithionate and thiocyanate concentrations at the end of the bottle roll experiments as a function of varying initial sulfite concentrations.

Figure 39 shows thiosulfate concentration change at the end of the bottle roll experiments versus sulfite concentration. Increasing the amount of sulfite salt added to the slurries, also increased ending thiosulfate concentration due to sulfite - polythionate reactions which produced more thiosulfate in leach solution as shown in Equations 36 – 38.

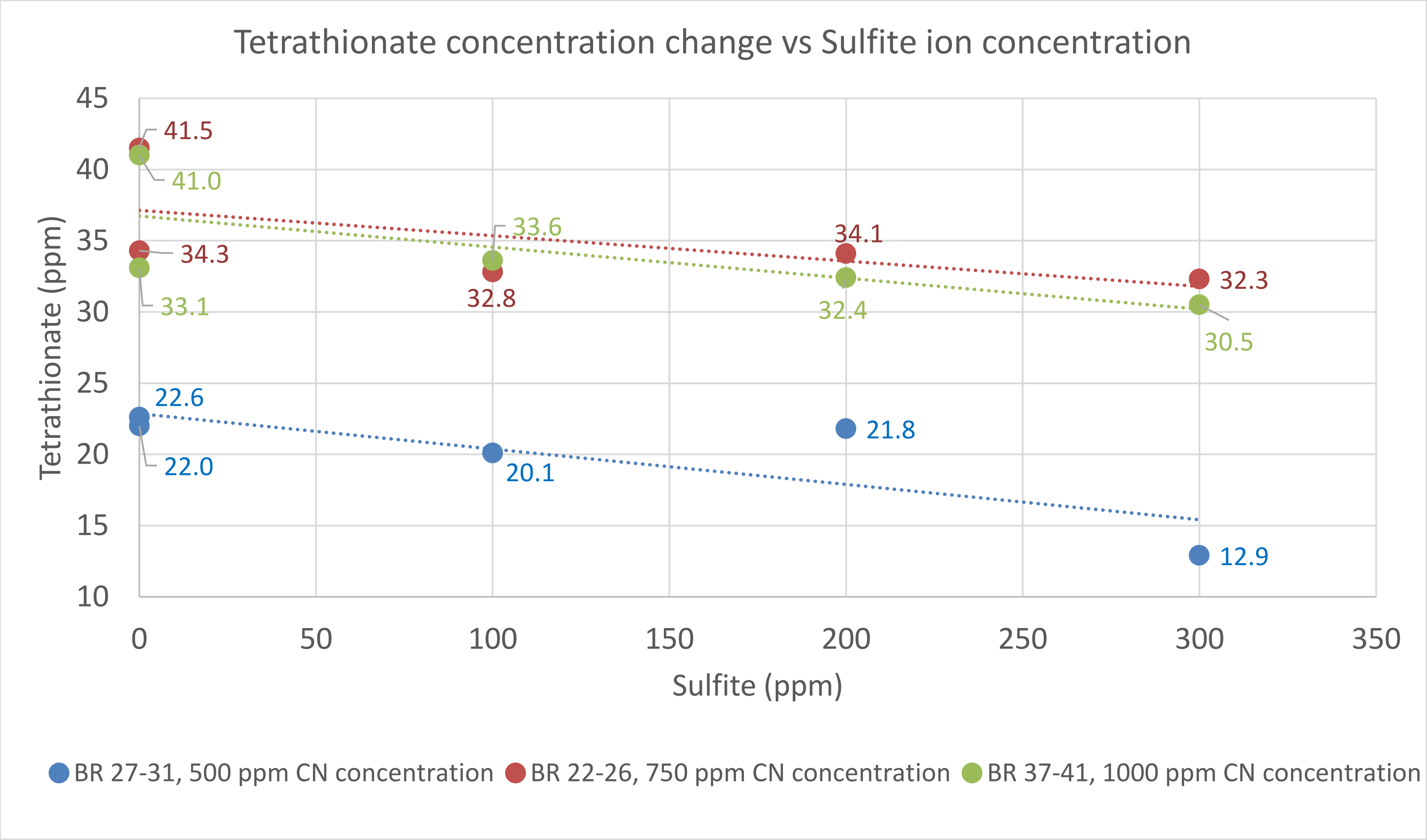


Figure 36. Tetrathionate Concentration Change vs Sulfite Ion Concentration

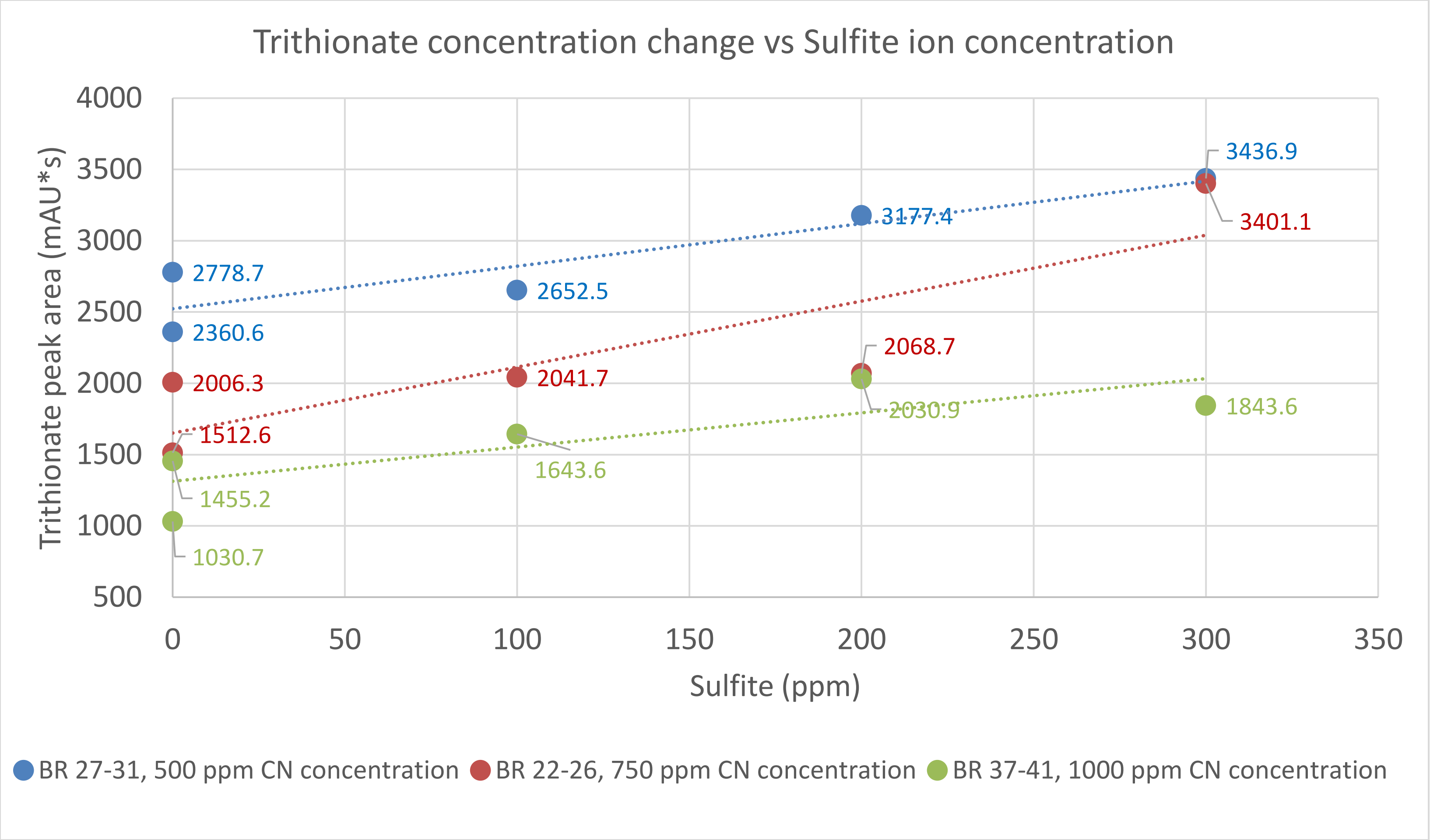


Figure 37. Trithionate Concentration Change vs Sulfite Ion Concentration

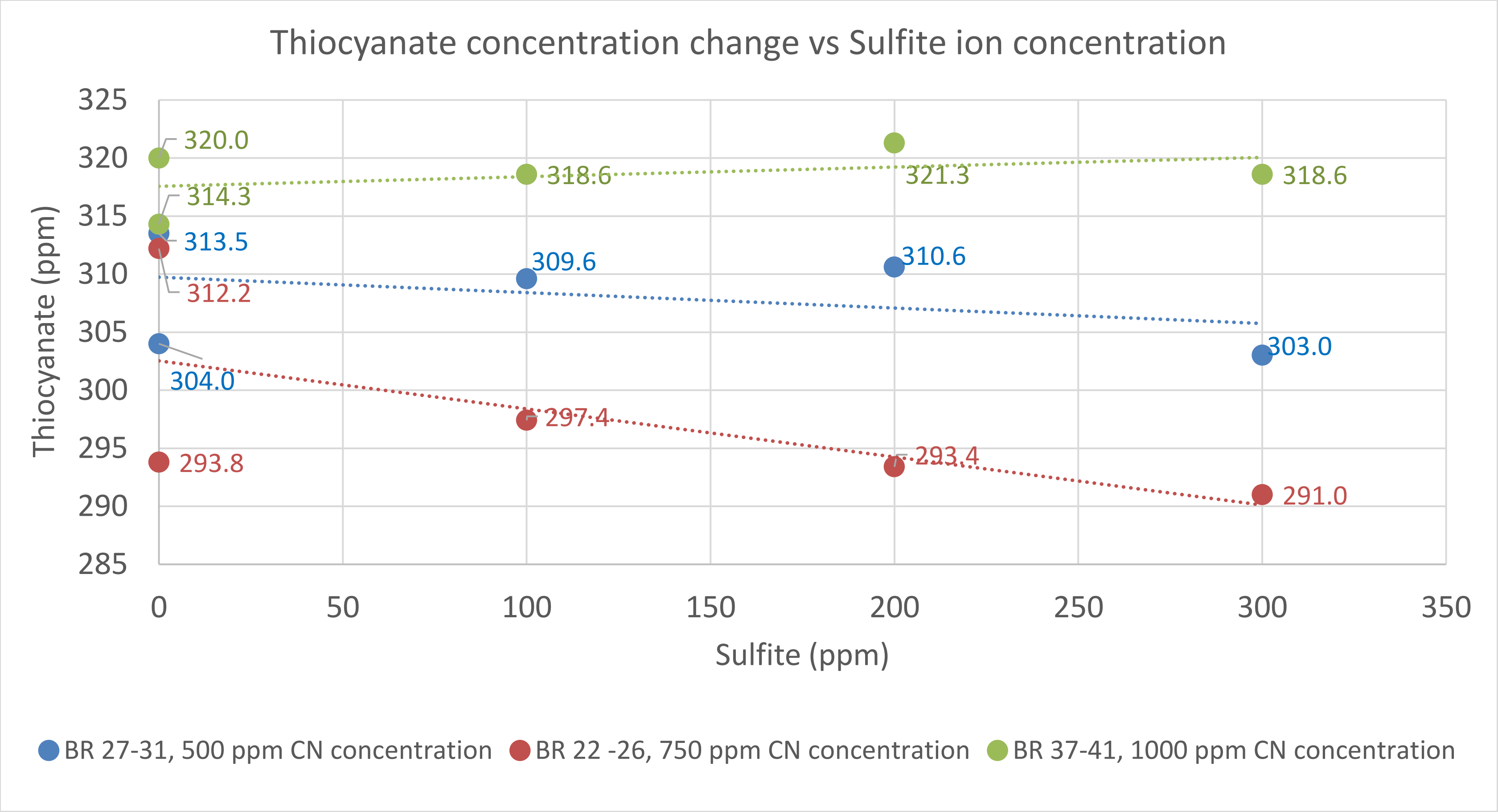


Figure 38. Thiocyanate Concentration Change vs Sulfite Ion Concentration

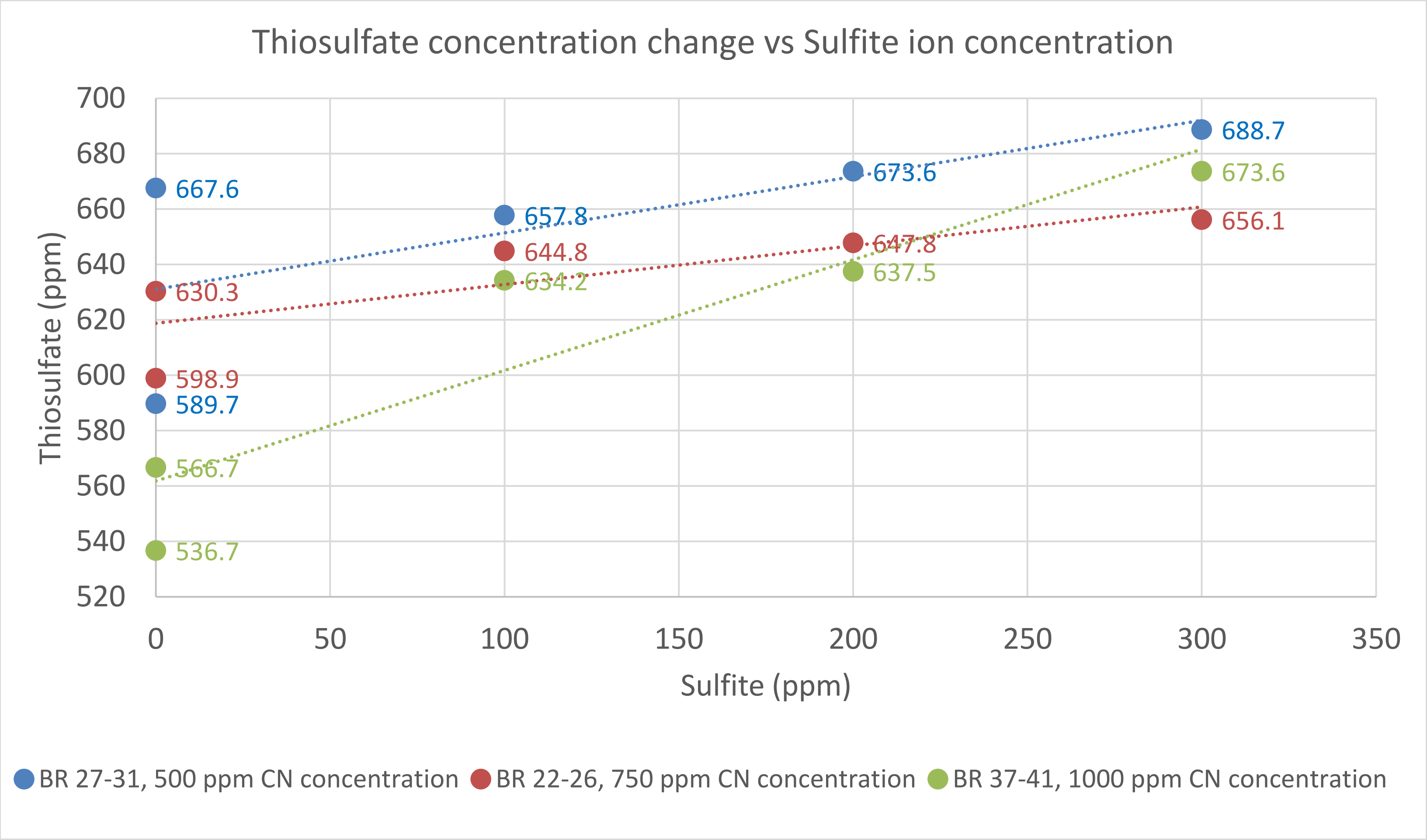


Figure 39. Thiosulfate Concentration Change vs Sulfite Ion Concentration

Figure 40 shows the direct relationship between ending tetrathionate, thiocyanate and initial cyanide concentrations. Bottle roll experiment results show that higher initial cyanide concentrations will result in higher amounts of both thiocyanate and tetrathionate formations at the end of the experiments.

The control experiments 27, 22 and 37 are the experiments conducted with initial cyanide concentrations of 500, 750, 1000 ppm without adding any other chemical other than lime. Results of these experiments showed that higher cyanide concentrations had higher ending thiocyanate concentrations. The increase in thiocyanate formation can be explained by reaction kinetics between cyanide and sulfur species.

As previously explained, polythionates react with free cyanide ions in leach solutions very rapidly by the Reactions 29 - 31,

$$CN^- + S_4O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + SCN^- + SO_4^{2-} + 2H^+ \tag{29}$$

$$2CN^- + S_5O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + 2SCN^- + SO_4^{2-} + 2H^+ \tag{30}$$

$$3CN^- + S_6O_6^{2-} + H_2O \leftrightarrow S_2O_3^{2-} + 3SCN^- + SO_4^{2-} + 2H^+ \tag{31}$$

Since the flotation tailings samples had a sulfide content of 10.98%, the only limiting reagent to form thiocyanate by the Reactions 29 - 31 was the free cyanide in leach solutions. Once the initial cyanide amounts were increased, ending thiocyanate formations also increased.

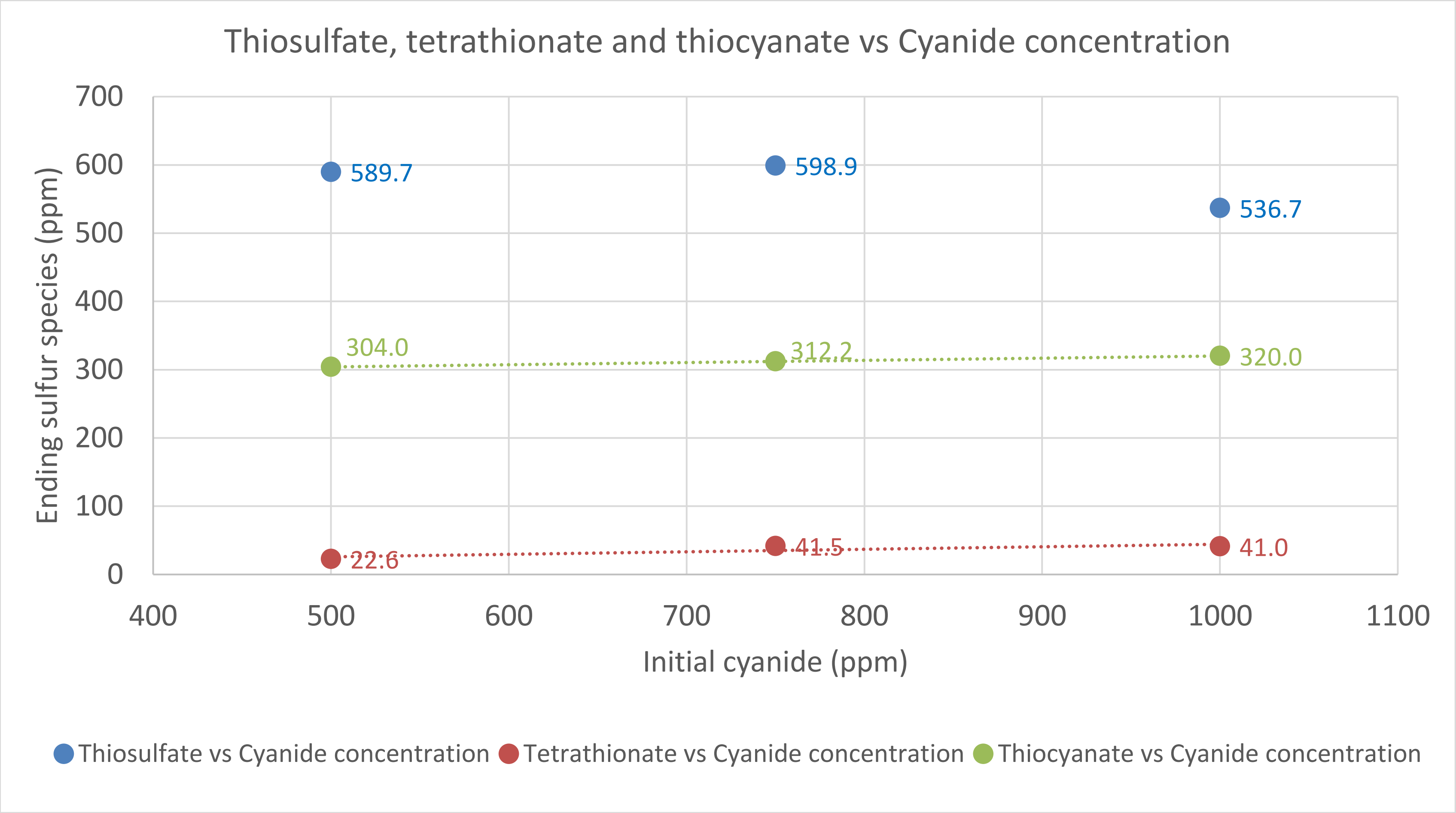


Figure 40. Thiosulfate, Tetrathionate and Thiocyanate vs Cyanide concentration

As Figure 40 indicates, cyanide-polythionate pathway can dominate over the cyanide-thiosulfate pathway during the formation of thiocyanate. Furthermore, the flotation tailings samples tested had 10.98% sulfide sulfur content and in such a high sulfide system within an alkaline solution, polythionates formed in leach slurries react with cyanide faster than thiosulfate to form thiocyanate.

Cyanide reacts with sulfide minerals which in turn increases the thiocyanate concentrations as well as the thiosulfate formations in leach solutions. At the same time, these reactions will also enhance the oxidation of reduced sulfur species. Since the polythionates are also the intermediate degradation products that form during oxidation of sulfide minerals, the increase in the tetrathionate concentrations by higher cyanide levels, as shown in Figure 40, can be explained by the thiosulfate oxidation to tetrathionate.

Additionally, as seen in Figure 40, there is no trend between the thiosulfate ion concentration and the increased amount of cyanide in solutions. The change in the concentration of anions such as polythionates, sulfite and sulfate contributes to the complexity to heterogenous kinetics of the leaching system. In addition to these complex interactions of the sulfur species by each other, thiosulfate and sulfate may associate with cations in leach solutions by the Equations 61 and 62 [107], [108] and may affect final concentration of thiosulfate ions.

$$Na^+ + S_2O_3^{2-} \leftrightarrow NaS_2O_3^- \qquad (61)$$

$$Na^+ + SO_4^{2-} \leftrightarrow NaSO_4^- \qquad (62)$$

As shown in the Figure 41, after increasing sulfite concentrations in leach solutions, cyanide consumptions were reduced because of the degradation of higher polythionates to trithionate while formed trithionate did not react with free cyanide as previously hypothesized.

Figure 41 also proves that there is a chemically optimum cyanide level for the sulfur-cyanide system since there was no more increase in WAD cyanide concentrations when the initial cyanide concentration in the solutions was set as 1000 ppm. However, both 500 and 750 ppm cyanide concentration conditions resulted in increased WAD cyanide concentrations by the increased amounts of sulfite salts in the leach solutions.

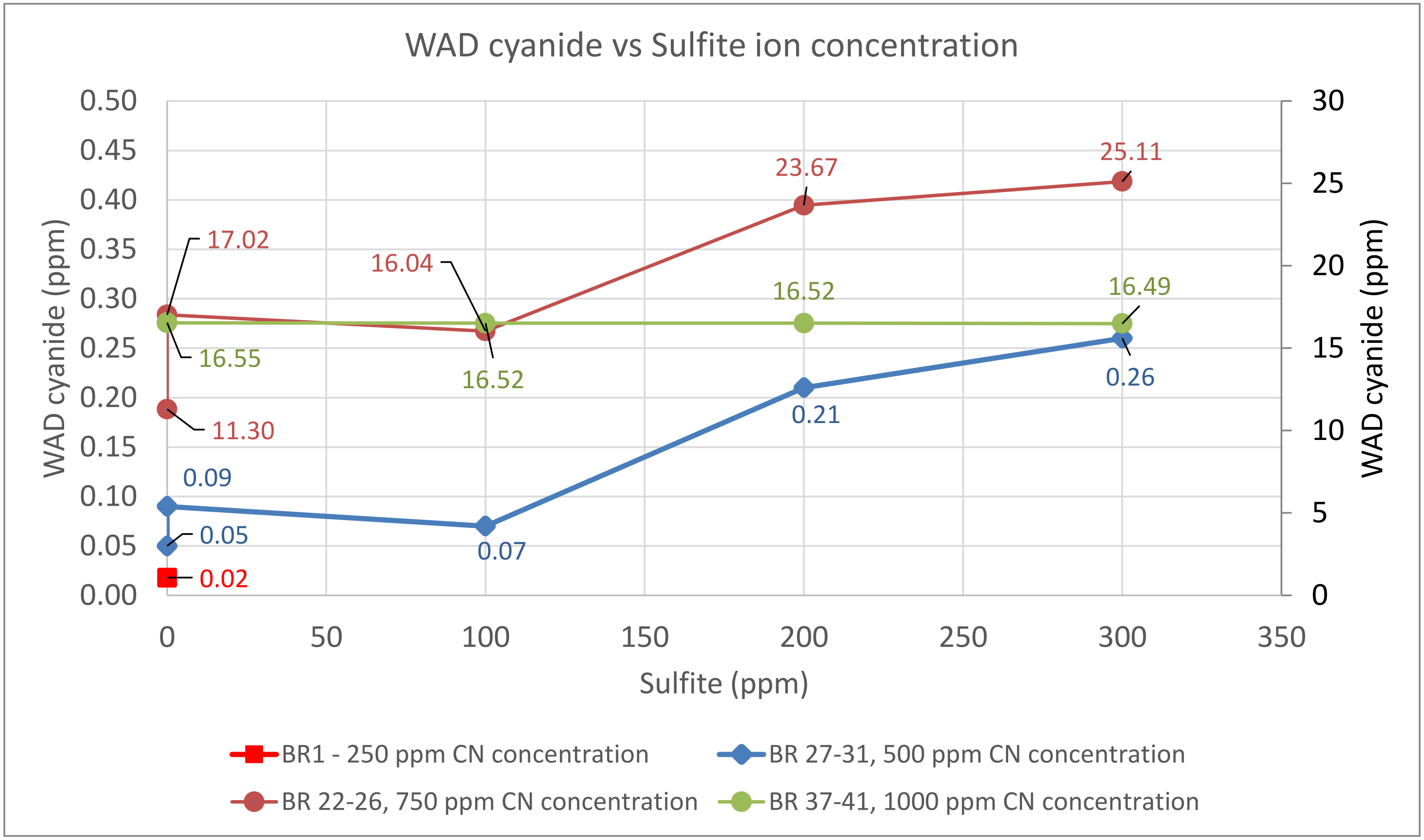


Figure 41. WAD Cyanide vs Sulfite Ion Concentration

Additional kinetic experiments were conducted for the bottle roll experiments 37-41 to observe change of sulfur species with time during the cyanide leaching. As shown in Figure 42 more than 90% of the thiosulfate formed during the first 4 hour of a 12 hr leach process at different sulfite concentrations with 1000 ppm initial cyanide concentration. Thiosulfate is a product of polythionate-cyanide, ploythionate-sulfite and hydrolysis reactions of polythionates. Thiosulfate also reacts with metal species in the leach solutions. Kinetics graph proves that most of these reactions complete during the first 4 hour of the bottle roil experiments.

Figure 43 shows that more than 95% thiocyanate forms during the first 8 hour of the leaching and thiocyanate concentration decreases with the increased sulfite concentrations. For the bottle roll experiments 37-41 where initial cyanide concentration 1000 ppm, ending thiocyanate concentration was lowest when the solution' initial sulfite concentration was the highest.

Figure 44 proves that the tetrathionate formation was lowest when the leach solution spiked with 300 ppm sulfite at the beginning of the bottle roll experiments. Tetrathionate kinetics graphs showed that nearly 50% and 75% of the tetrathionate forms during the first 4 and 8 hours, respectively.

As hypothesized, trithionate concentrations increased mainly because of the reactions between polythionates and sulfites. The trithionate concentration change based on the sulfite concentrations are shown in Figure 45.

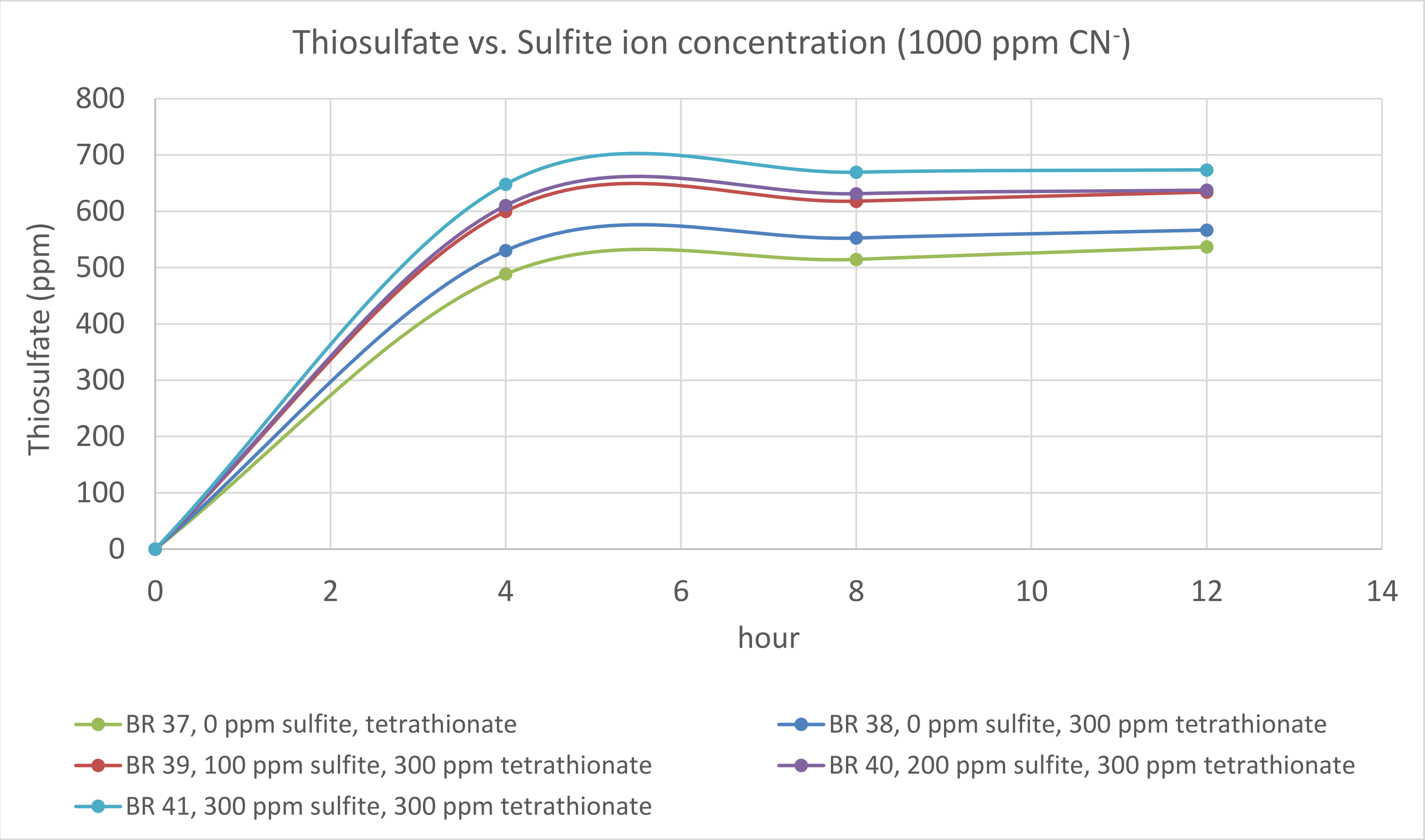


Figure 42. Thiosulfate vs. Sulfite Ion Concentration

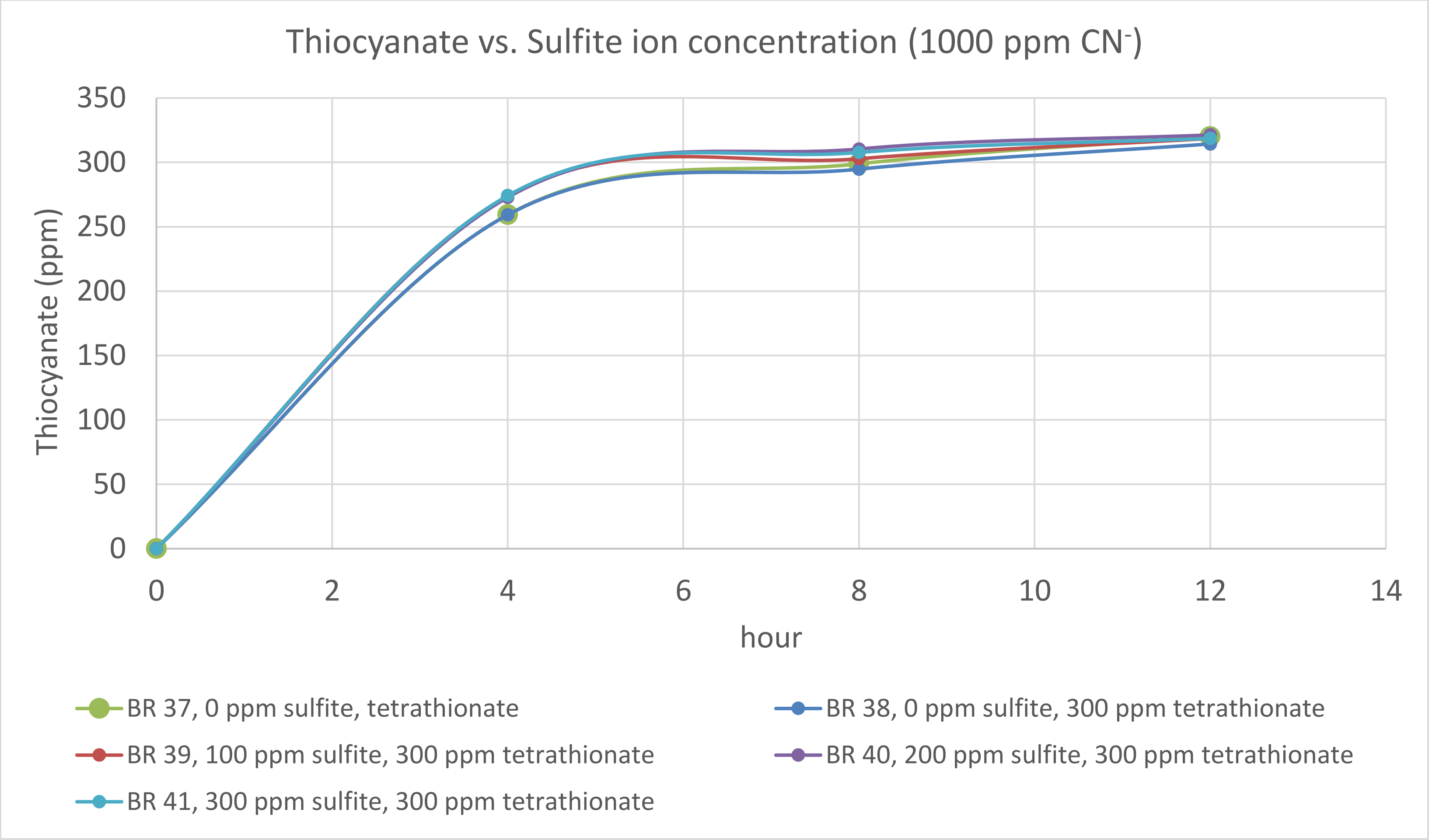


Figure 43. Thiocyanate vs. Sulfite Ion Concentration

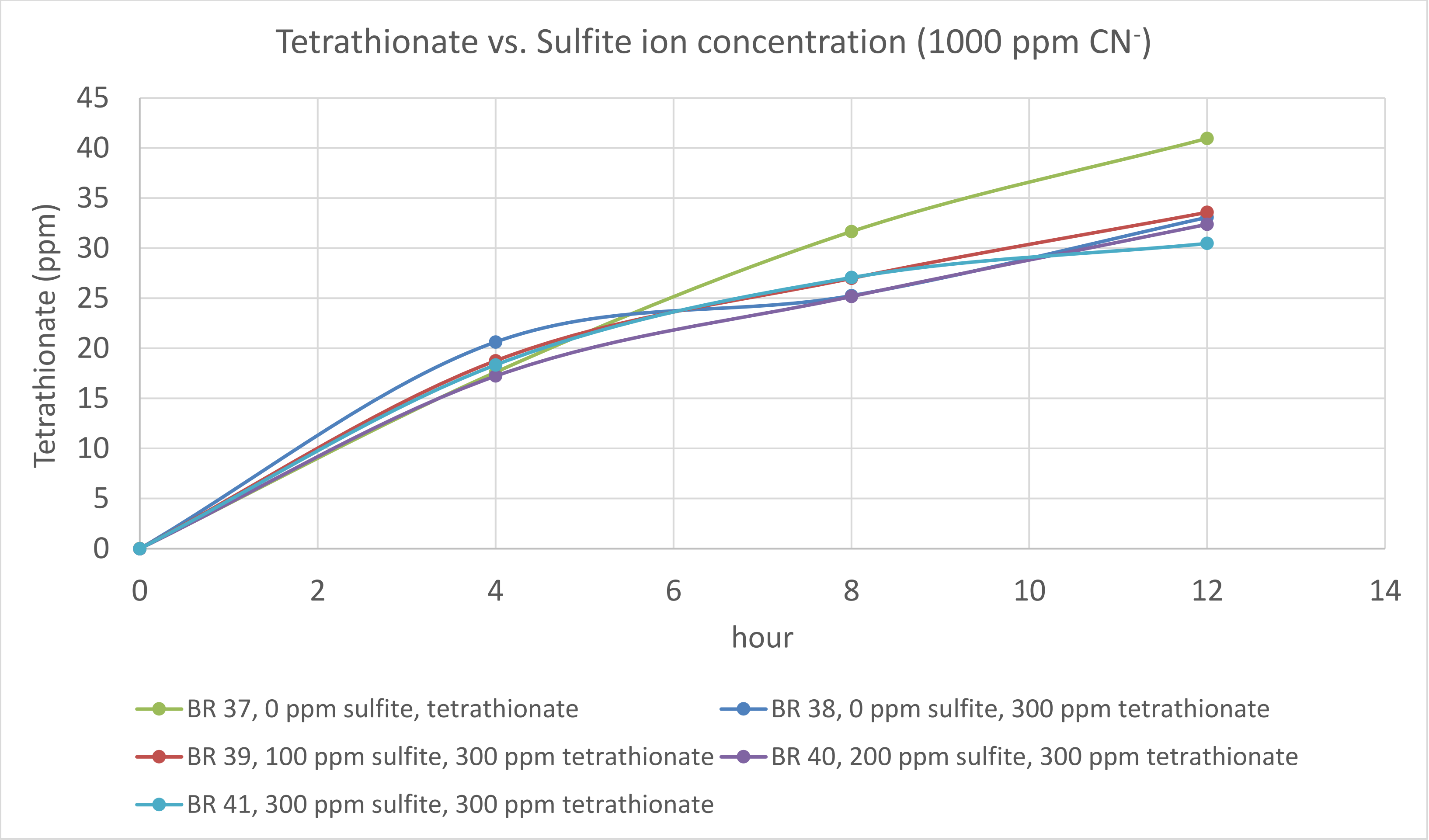


Figure 44. Tetrathionate vs. Sulfite Ion Concentration

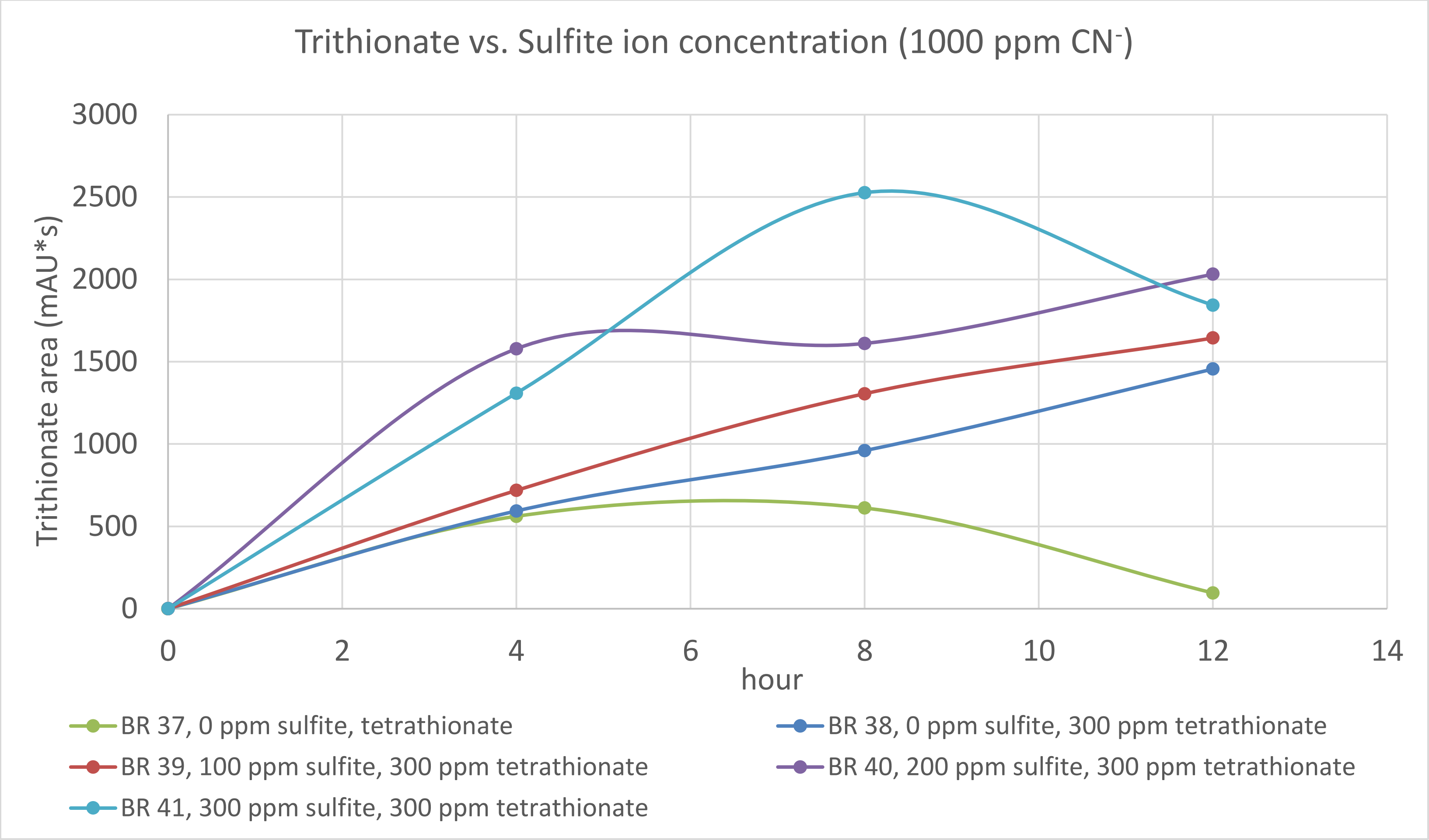


Figure 45. Trithionate vs. Sulfite Ion Concentration

At 25 ^oC, H_2S, HS^-, SO_4^{2-} are the stable sulfur species formed in alkaline solutions whereas thiosulfates, sulfites and polythionates are accepted as metastable species [109]. In order to have more information about the natural degradation of the tetrathionate, thiosulfate and thiocyanate under laboratory conditions, some of the clear leach solutions were analyzed with two-hour delay. Figure 46 shows the tetrathionate degradation in 2-hour period.

Bottle roll experiment 37 which was conducted without addition of sulfite resulted in a 20% decrease in tetrathionate concentration within two (2) hours. However, the experiment 41 where 300 ppm sulfite was added to the leach solution resulted in 7% decrease in tetrathionate concentration after two (2) hours. Since the natural degradation of sulfur species was expected at the beginning of the experiments, each bottle roll sample was analyzed in less than half an hour time frame.

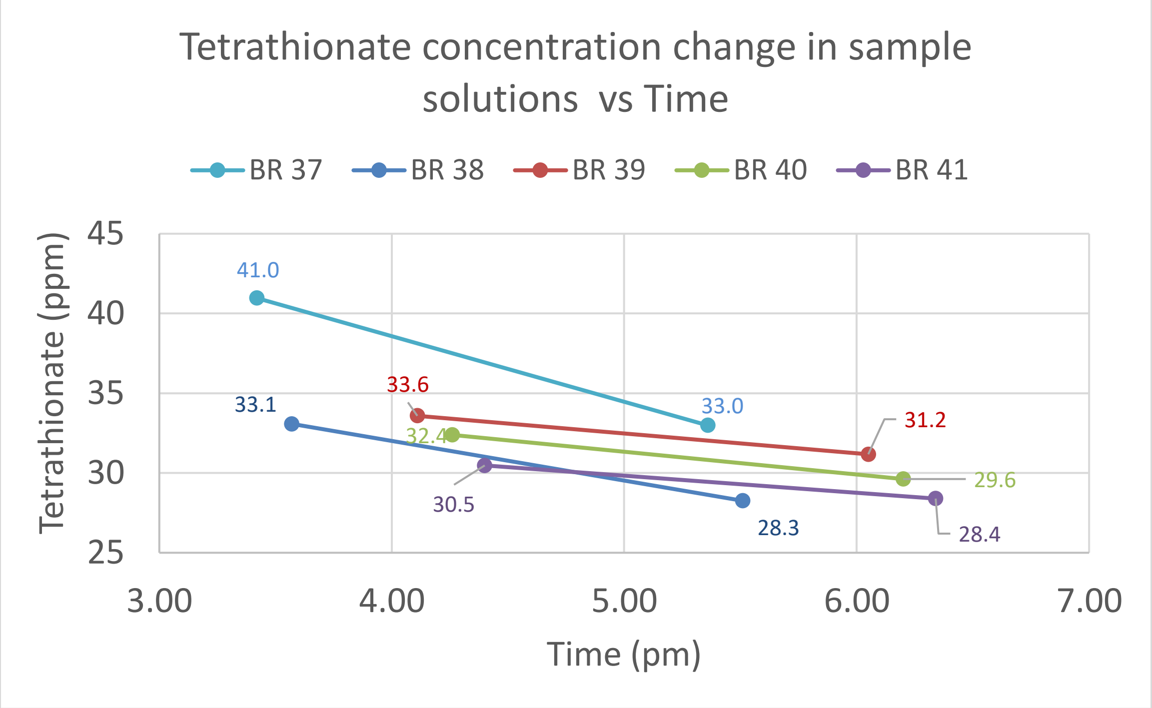


Figure 46.Tetrathionate Concentration Change in Sample Solutions vs Time

Figure 47 and Figure 48 show the thiosulfate and thiocyanate concentration change in the same leach solution between two measurements with two (2) hour delays.

As shown in Figure 47, natural degradation of thiosulpfate is slower compared to tetrathionate. Thiosulfate concentrations decreased 3% on average at the end of the two (2) period.

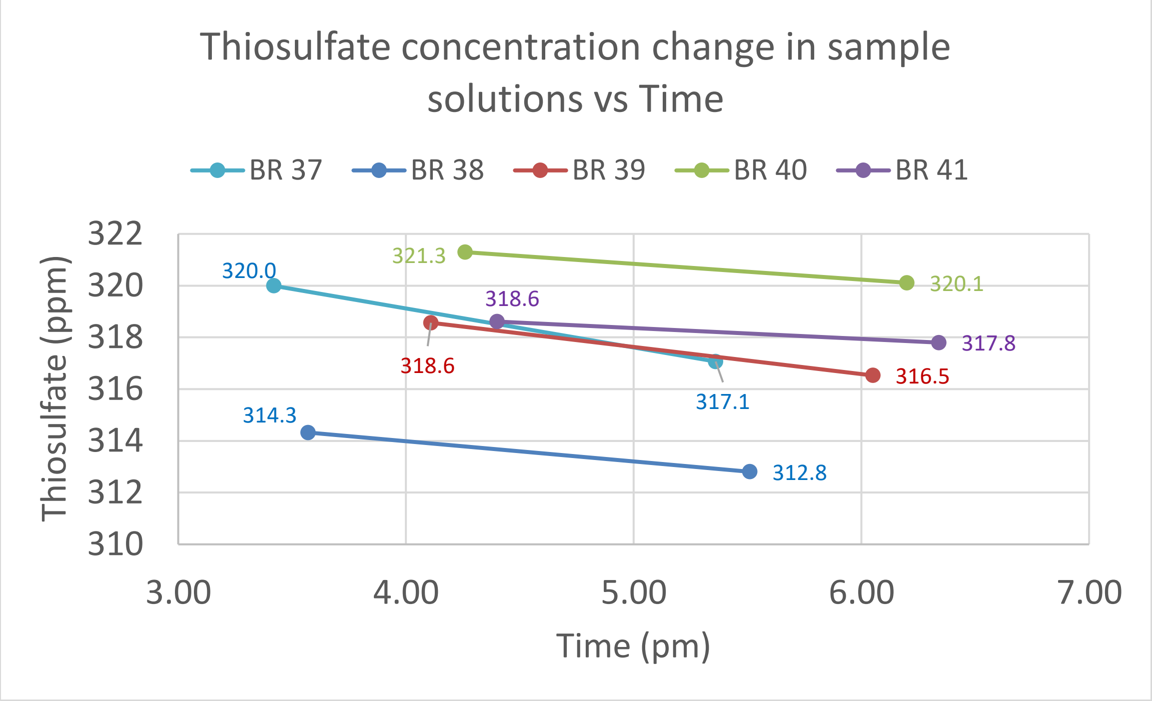


Figure 47. Thiosulfate Concentration Change in Sample Solutions vs Time

The change in thiosulfate concentration in clear leach solutions may be caused by its oxidation. Possible oxidation products of the thiosulfate are trithionate and sulfate. The thiosulfate degradation to trithionate is represented in below reaction steps [110],

$$S_2O_3^{2-} + O_2 \leftrightarrow S_2O_5^{2-} \quad (63)$$

$$2S_2O_5^{2-} \leftrightarrow S_2O_6^{2-} + S_2O_4^{2-} \quad (64)$$

$$S_2O_6^{2-} + S_2O_4^{2-} \leftrightarrow S_3O_6^{2-} + SO_4^{2-} \quad (65)$$

$$2S_2O_5^{2-} \leftrightarrow S_3O_6^{2-} + SO_4^{2-} \quad (66)$$

Overall reaction can be summarized as follows,

$$S_2O_3^{2-} + O_2 \leftrightarrow 0.5\ S_3O_6^{2-} + 0.5\ SO_4^{2-} \tag{67}$$

Thiocyanate concentration change in clear sample solutions is shown in Figure 48. Thiocyanate ions are the most stable species compared to thiosulfate and tetrathionate. Thiocyanate concentration in sample solutions stayed nearly same at the end of two (2) hour period.

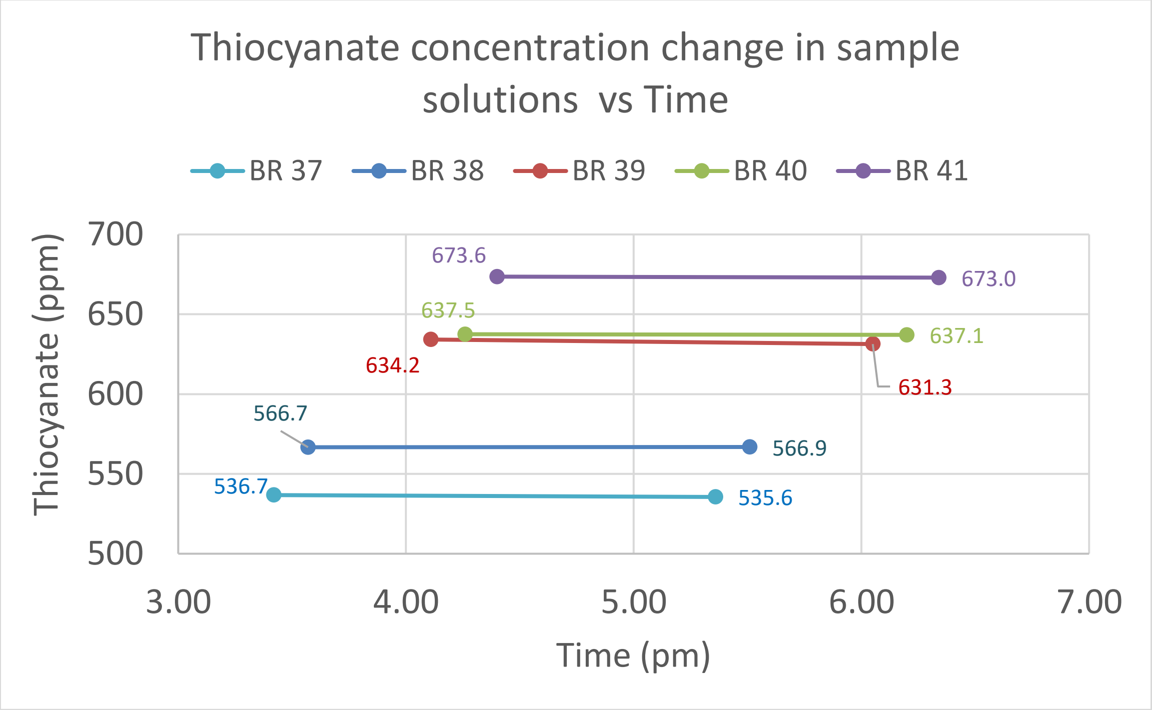


Figure 48. Thiocyanate Concentration Change in Sample Solutions vs Time

4.4 METAL RECOVERIES

In order to calculate the metal recoveries, metal head assays were calculated for each bottle roll experiment based on the following formula,

$$\left[Dissolved\ metal\ \left(\frac{mg}{L}\right) * \frac{Sol.Vol.(ml)}{Solid\ weight\ (gr)} * \frac{1\ L}{1{,}000\ ml} * \frac{1\ gr}{1{,}000\ mg} * \frac{1{,}000{,}000\ gr}{1\ MT} * \frac{\left(0.0292\frac{oz}{st}\right)}{(1\ ppm)}\right] + \left[Metal\ assay\ in\ tailings\ \left(\frac{oz}{st}\right)\right] \tag{68}$$

Metal recoveries were calculated based on calculated head assays and tailings' metal assay content,

$$\left[\frac{(Calculated\ metal\ head\ assay - Metal\ assay\ in\ tailings)}{(Calculated\ metal\ head\ assay)} * 100\right] \tag{69}$$

Since the head assays were recalculated by using dissolved metal in leach solutions and metal content of the tailings, a head assay accountability value for each bottle roll experiment was also determined. Average accountabilities for gold, silver and copper head assays were 115%, 97% and 91%, respectively. Accountabilities calculated by the following formula,

$$\left[\frac{(Calculated\ metal\ head\ assays)}{(Sample\ metal\ head\ assay)} * 100\right] \tag{70}$$

Accountability values for each experiment are provided in Appendix A.

Before starting each bottle roll experiment, weights of the bottle, bottle and solid, bottle, solid sample and water were measured separately and recorded to avoid any slurry percent solid errors. These values are also shown in Appendix B.

The ending reduced sulfur species concentration, WAD cyanide and metal recoveries of each bottle roll experiment are presented in Table 45. Results showed that metal recoveries increased with increased amounts of SO_3^{2-} concentrations in the solutions, since there was more WAD cyanide in leach solutions and adverse effects from higher polythionates such as film forming around lixiviants ions or metal surfaces diminished.

Figures 49, 50 and 51 shows the gold, silver and copper recovery changes versus cyanide and sulfite concentrations. The results of the duplicate experiments are shown in Appendix B.

Gold and silver solubility may also have increased as a result of formation of thiosulfate and bisulfide ligands in the systems $Au\text{-}S\text{-}O_2\text{-}H_2O$ and $Ag\text{-}S\text{-}O_2\text{-}H_2O$. In alkaline solutions, gold and silver form stable complexes such as $Au(S_2O_3)_2^{3-}$, $Au(HS)$ and $Ag(S_2O_3)_2^{3-}$, $AgHS^0$, $Ag(HS)_2^-$, respectively.

Addition of sulfite into the leach solution also causes formation of two mixed thiosulfate-sulfite complexes which are in equilibrium with gold thiosulfate complex [116].

$$Au(S_2O_3)_2^{3-} + SO_3^{2-} \leftrightarrow Au(S_2O_3)(SO_3)^{3-} + S_2O_3^{2-} \qquad (K=1.09) \qquad (71)$$

$$Au(S_2O_3)_2^{3-} + 2SO_3^{2-} \leftrightarrow Au(S_2O_3)(SO_3)_2^{5-} + S_2O_3^{2-} \qquad (K=4.8) \qquad (72)$$

The formation of the gold-thiosulfate complexes may also be affected by the presence of the other metal thiosulfate complexes because of the gold's affinity to form mixed metal complexes such as $(Au, Ag)(S_2O_3)_2^{3-}$. Gold also forms complexes such as $Au(HS)_2^{-}$, AuS^{-} and $Au_2(HS)_2S^{2-}$ with sulfur species [112]. During the bottle roll experiments, different intermediate sulfur products has formed and some of these species further oxidized to sulfate. Formation of the sulfate in the leach solutions enhanced the gold dissolution kinetics by depressing the sulfide dissolution in slurries [113].

Gold dissolution rate is adversely affected by release of copper into the leach solutions after dissolution of the sulfide minerals in solutions since this causes decrease in dissolved oxygen in leach solutions and higher oxidation potential. At the same time copper release enhances gold dissolution by causing higher solution potential in the slurries. In this experimental system, the dissolution of gold and silver in the presence of thiosulfate ions was slow [114] but catalytic actions of copper ions have been found to increase the gold dissolution rate [115]. At the same time, copper ions in leach solutions consume thiosulfate and forms copper thiosulfate complexes in the solutions and as well as insoluble copper sulfide in the tailings.

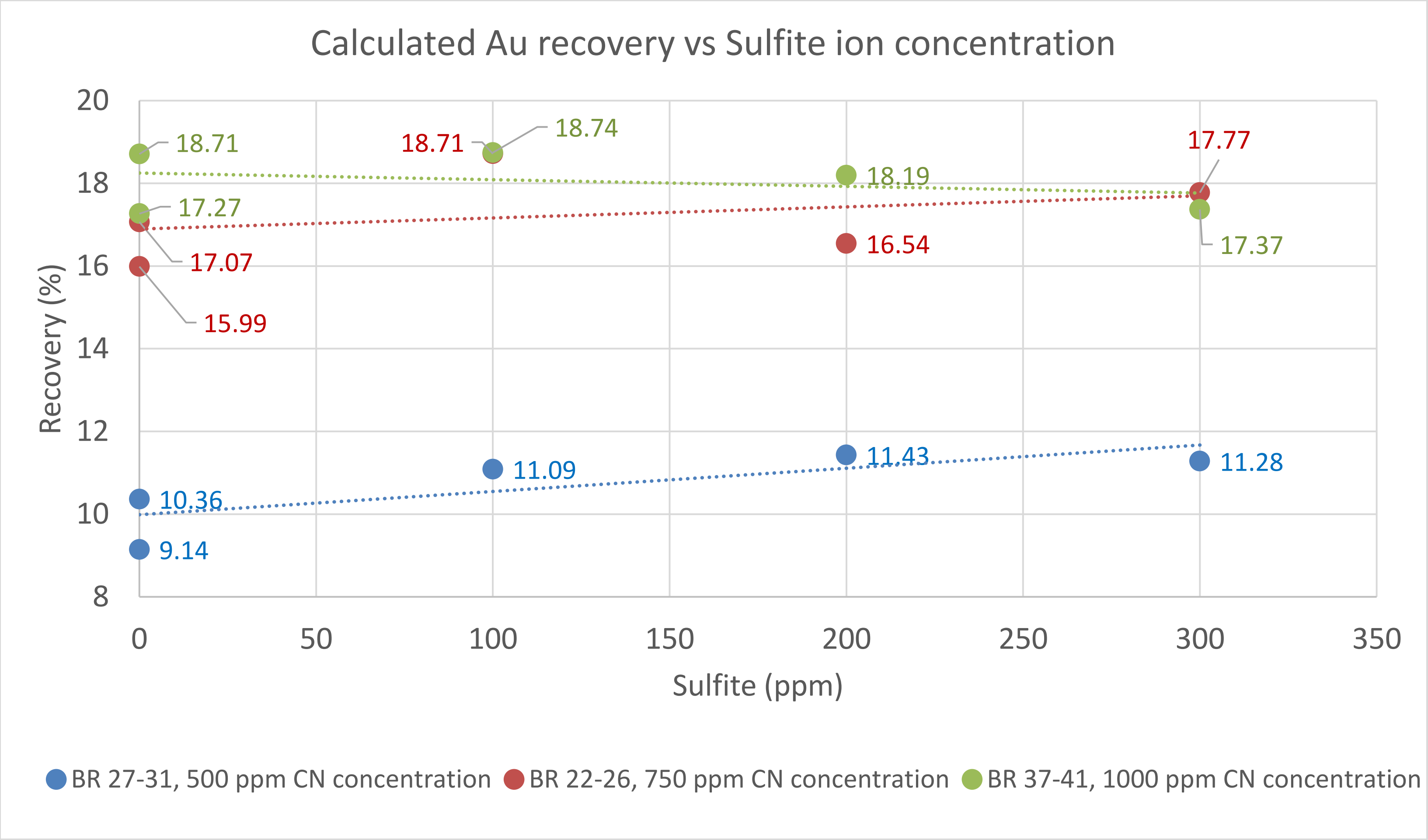


Figure 49. Au Recovery vs Sulfite Ion Concentration

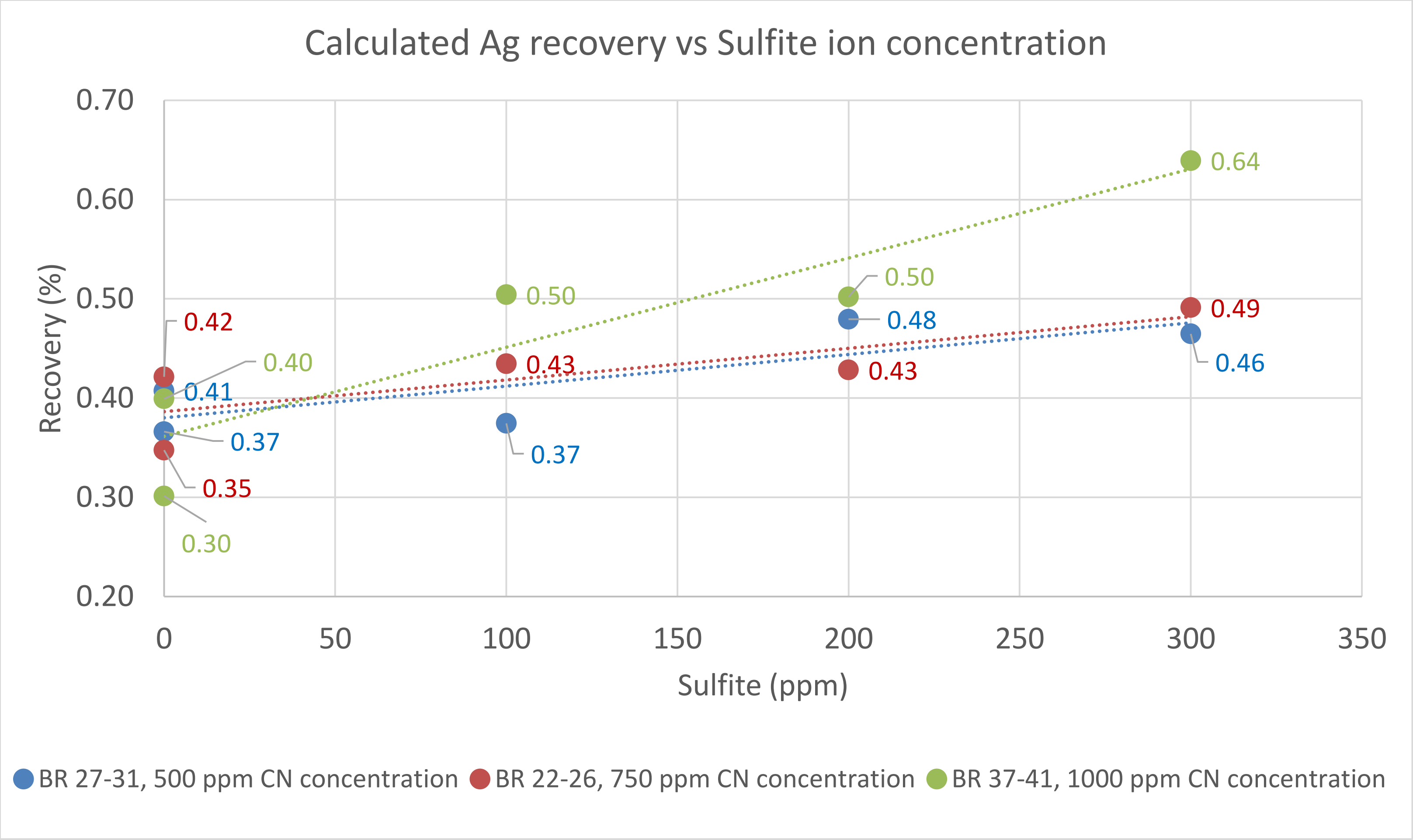


Figure 50. Calculated Ag Recovery vs Sulfite Ion Concentration

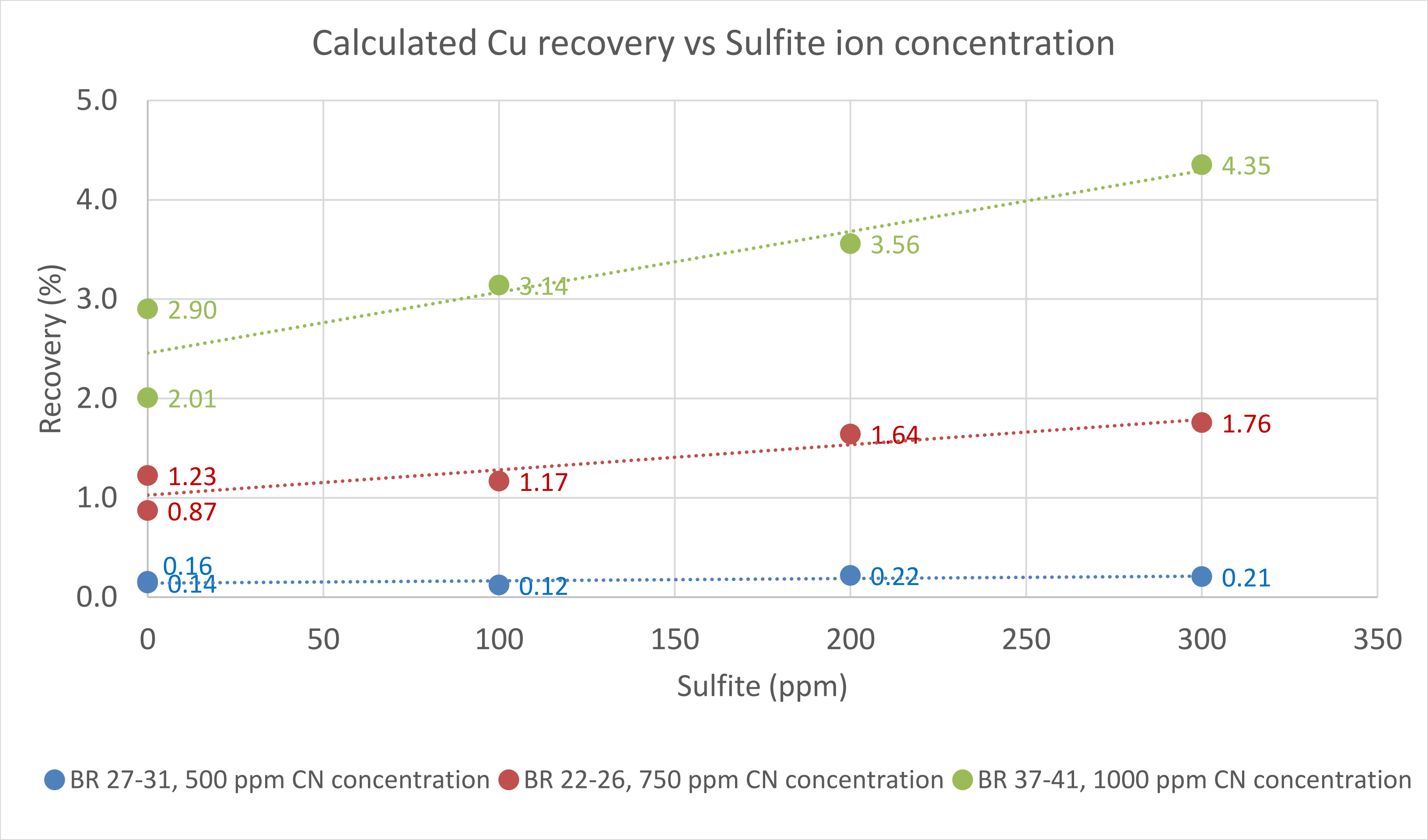


Figure 51. Calculated Cu Recovery vs Sulfite Ion Concentration

A varying increase (5-20%) in the metal recoveries was observed after spiking the leach solutions with tetrathionate without addition of sulfite salts. This may be explained by the formation of thiosulfate in the solutions by hydrolysis of tetrathionate ion and the increase in the metal thiosulfate complexes in the leach solutions. Tetrathionate hydrolyses to trithionate and thiosulfate as shown in Equation 34 [111].

$$4\ S_4O_6^{2-} + 6\ OH^- \leftrightarrow 5\ S_2O_3^{2-} + 2\ S_3O_6^{2-} + 3\ H_2O \qquad (34)$$

Ending metal recoveries, dissolved metal and tailing’s metal content for each bottle roll experiments versus cyanide and sulfite concentration are presented in Appendix A. Average results of the duplicates from each experimental set is presented in Table 46. These results are the comparison of experiments to the control experiment in each set and were obtained by averaging the results of the duplicate experiments.

As shown in the Table 46, initial mix of 500 ppm cyanide and 300 ppm sulfite concentration is the optimum level for the flotation tailings tested. At 1000 ppm cyanide levels, gold recovery changes decreased and silver recovery changes increased compared to the 500 and 750 ppm initial cyanide levels. An increase in cyanide concentration also increases the gold recoveries up to a critical cyanide value. Above this critical value gold recoveries do not increase anymore. Depending on the amount of the impurities in solid samples, cyanide concentrations higher than critical level causes adverse effects on gold recovery.

Concentration of cyanide also affects the sulfur speciation. High cyanide concentration may also have resulted in formation of sulfur species which has not investigated through this study and these species may have caused adverse effects such as film forming around the gold particles affecting gold-cyanide interactions.

Initial NaCN (ppm)	Initial SO_3^{2-} (ppm)	Avg. Au Rec. change (%)	Avg. Ag Rec. change (%)	WAD cyanide (ppm)	SCN^- conc. change (%)	$S_4O_6^{2-}$ conc. change (%)	$S_3O_6^{2-}$ conc. change (%)	$S_2O_3^{2-}$ conc. change (%)
500	100	11.1	14.9	0.13	0.8	- 6.1	22.7	9.4
500	200	9.8	32.3	0.15	- 0.1	- 8.9	37.8	12.3
500	300	13.3	28.8	0.21	- 1.5	- 44.9	45.3	14.0
750	100	11.0	26.0	16.67	- 7.9	- 26.9	60.7	7.8
750	200	11.8	24.4	23.65	- 8.9	- 22.9	68.2	8.3
750	300	10.4	41.9	25.08	- 19.9	- 28.3	119.7	10.6
1000	100	6.5	66.9	16.50	-1.4	- 23.4	99.1	14.1
1000	200	4.4	63.1	16.48	- 2.5	- 24.8	121.2	15.2
1000	300	4.7	92.8	16.46	- 3.4	- 25.8	122.6	20.3

Table 46. Experiment Results

At 1000 ppm initial cyanide concentration level, silver recovery change increased more than the 500 and 750 ppm initial cyanide concentration levels. At the same time, higher thiosulfate and dissolved copper in leach solutions did not increase gold recovery changes. This can be explained by reaction rate difference of thiosulfate with gold and silver. At 1000 ppm cyanide level both dissolved copper and thiosulfate concentrations in the solutions was highest. Since the dissolved copper is a catalyst for thiosulfate leaching and there were high amounts of thiosulfate present in the leach solution, silver recovery changes increased as much as two and a half times compared to the lower initial cyanide concentrations. Silver-thiosulfate reaction rate is almost seven times higher compared to gold-thiosulfate [117]. As a result of this, available thiosulfate in leach solutions initially consumed during the silver leaching process.

5. CONCLUSION

The conducted research aimed to investigate the main sulfur species affecting cyanide consumption and metal dissolutions during cyanide leaching. The results showed that it is possible to increase available cyanide levels in leach solutions, and gold and silver recoveries by sulfite addition during leaching of sulfide ores after controlling the tetrathionate levels in slurries. Increasing the sulfite concentration in leach solutions lowered tetrathionate and thiocyanate levels, increased trithionate and available cyanide concentrations resulting in higher gold and silver recoveries.

Based on the experimental results, initial mix of 500 ppm cyanide and 300 ppm sulfite concentration was found to be the optimum level for lowering cyanide consumption as well as for the gold and silver recoveries. At 500 ppm cyanide and 300 ppm sulfite concentrations, average gold and silver recoveries increased 13.3% and 28.8%, respectively and available cyanide concentration increased four times compared to the control experiments.

The kinetics data obtained from the experiments conducted with 500 and 750 ppm initial cyanide concentration indicated that the addition of sulfite increases the available cyanide in leach solutions spiked with tetrathionate. However, sulfite ion concentrations had less effect on gold recoveries and no effect on available cyanide in leach solutions when initial cyanide concentration was 1000 ppm. At 1000 ppm cyanide level, gold recovery changes decreased, and silver recovery changes increased at each sulfite concentration level compared to the experiments conducted with 500 and 750 ppm cyanide concentrations. Since 1000 ppm initial cyanide concentration was above the critical cyanide level, gold and silver leaching by cyanide slowed and most of the silver leached at this cyanide level was due to the thiosulfate leaching. This finding proved that there is an optimum cyanide-sulfite concentration point for the flotation tailing samples at which reagent consumptions could be minimized and net economical value of the metals recovered could be maximized.

The formation of the thiosulfate and thiocyanate through polythionate cyanolysis is dependent on the amount of free cyanide available in leach solutions. Polythionates cause thiocyanate formation in cyanide solutions more than the other sulfur species. In order to observe the kinetics of the sulfur species formation and the extent of their reactions with cyanide, additional kinetic analyses were conducted. Kinetic curves of the formed sulfur species showed that more than 75% of thiocyanate, 90% of thiosulfate and 50% of tetrathionate formed during the first four hours of the twelve-hour bottle roll leach experiments. Kinetic experiments also showed that tetrathionate degraded nearly 20% and thiocyanate concentrations stayed nearly same in clear leach solutions at the end of two-hour period.

6. FUTURE WORK

Experiments resulted in important findings on kinetics of the reduced sulfur species in cyanide leaching solutions and their effects on gold and silver recoveries. However, samples with different gold, silver and sulfur content should also be leached under the same experimental conditions to get a better picture on optimum cyanide-sulfite concentration level parameters and reaction kinetics based on metal and sulfur content of the samples.

Additional experiments should be conducted with high sulfide sulfur (>10%) flotation tailings samples where the slurries are pretreated with dissolved oxygen prior to leaching. Following the pretreatment, cyanide leaching experiments should be conducted by feeding oxygen to the leach solutions and the changes in sulfite and reduced sulfur reaction kinetics should be analyzed.

Duration of sulfite - slurry pre-mixing should be optimized to maximize the reactions between the sulfite and sulfur species during this period.

The gold complexes, e.g. gold-thiosulfate, gold-cyanide, in leach solutions should be analyzed separately to quantify more accurately the amount of gold leached by cyanide.

7. REFERENCES

[1] J. Byerley, S. Fouda and G. Rempel, "J. Chem. Soc.," *Kinetics and Mechanism of the Oxidation of Thiosulfate Ions by Copper(II) Ions in Aqueous Ammonia Solution,* pp. 889-893, 1973.

[2] M. Aylmore and D. Muir, "Thiosulfate Leaching of Gold: A Review," *Mineral Engineering,* vol. 14, no. 2, pp. 135-174, 2001.

[3] G. Deschenes, C. Xia, M. Fulton, L. Cabri and J. Price, "Evaluation of Leaching Parameters for a Refractory Gold Ore Containing Aurostibnite and Antimony Minerals: Part I – Central Zone," *Minerals Engineering,* vol. 22, no. 9-10, pp. 799-808, 2009.

[4] F. Habashi, "Kinetics and Mechanicsm of Gold and Silver Dissolution in Cyanide Solution," State of Montana, Breau of Mines and Geology, Butte, 1967.

[5] G. Senanayake, "The Cyanidation of Silver Metal: Review of Kinetics and Reaction Mechanism," *Hydrometallurgy,* vol. 28, no. 2, pp. 693-702, 2006.

[6] T. Austad, "Polythionates. I. The Reaction Between the Tetrathionate Ion and the Cyanide Ion in Acetonitrite," *Acta Chemica Scandinavica,* vol. 28, no. 1974, pp. 693-702, 1974.

[7] E. Wilberg, N. Wiberg and A. Holleman, Inorganic Chemistry, San Diego: Academic Press, 2001.

[8] A. Roy and P. Trudinger, The Biochemistry of Inorganic Compounds of Sulphur, Cambridge: University Press, 1970.

[9] D. Lyons and G. Nickless, "The Lower Oxy-Acids of Sulphur," in *Inorganic Sulphur Chemistry*, Amsterdam, Elsevier, 2001, pp. 135-174.

[10] C. Moses, D. Nordstrom, J. Herman and A. Mills, "Geochimica et Cosmochimica Acta," *Aqueous Pyrite Oxidation by Dissolved Oxygen and by Ferric Iron,* vol. 51, no. 6, pp. 1561-1571, 1987.

[11] X. Chen, X. Lan, Q. Zhang and J. S. Y. Zhou, "Behavior of S_2O_3 and SO_3^{2-} in Sulfur Bearing Aqueous Solution System for Gold Leaching," *Transactions of Nonferrous Metals Society of China,* vol. 20, no. 2010, pp. 46-49, 2009.

[12] B. Meyer, Elemental Sulfur, Berkeley: University of California, Berkeley, 1972.

[13] C. Housecroft and A. Sharpe, Inorganic Chemistry, Saddle River, NJ: Pearson, 2014.

[14] "ChEBI:15138 - Sulfide," ChEBI, [Online]. Available: https://www.ebi.ac.uk/chebi/chebiOntology.do?chebiId=CHEBI:15138. [Accessed 18 February 2017].

[15] N. Greenwood and A. Earnshaw, Chemistry of the Elements, Leeds, England: Butterworth-Heinemann, 1997.

[16] S. Chryssoulisa and J. McMullenb, "Mineralogical Investigation of Gold Ores," *Developments in Mineral Processing,* vol. 15, pp. 21-71, 2005.

[17] "Some Sulfides of Gold and Silver: Composition, Mineral Assemblage, and Conditions of Formation," *Theoretical Foundations of Chemical Engineering,* vol. 42, no. 5, p. 411–421, 2008.

[18] J. Marsden and L. House, The Chemistry of Gold Extraction, Littleton: Society of Mining, Metallurgy and Exploration Inc., 2006.

[19] H. M. Michael Fleet, "Gold-Bearing Arsenian Pyrite and Marcasite and Arsenopyrite from Carlin Trend Gold Deposits and Laboratory Synthesis," *American Mineralogist,* vol. 82, pp. 182-193, 1997.

[20] J. Marsden and L. House, Chemistry of Gold Extraction, Littleton: Society of Mining, Metallurgy and Exploration Inc., 2006.

[21] J. W. Anthony, R. A. Bideaux, K. W. Bladh and M. C. Nichols, Handbook of Mineralogy, Tucson: Mineral Data Publ., 1995.

[22] A. Piestrzynski, Mineral Deposits at the Beginning of the 21st Century, Lisse: A.A. Balkema, 2001, p. 511.

[23] T. Williams, A. J. Michael Gunn, P. Harvey and P. Tittes, "The Application of Geobiotics and Geocat Technology to the Bacterial Oxidation of a Refractory Arsenopyrite Gold Concentrate," in *Hydrometallurgy 2008: Proceedings of the Sixth International Symposium*, Littleton, 2008.

[24] I. Y. Nekrasov, Geochemistry, Mineralogy and Genesis of Gold Deposits, Moscow: Balkema Publishers, 1996.

[25] G. Deschenes, C. Xia, M. Fulton, L. Cabri and J. Price, "Evaluation of Leaching Parameters for a Refractory Gold Ore Containing Aurostibite and Antimony Minerals: Part I – Central Zone," *Minerals Engineering,* vol. 22, no. 9-10, pp. 799-808, 2009.

[26] "Aurostibite Mineral Data," [Online]. Available: http://webmineral.com/data/Aurostibite.shtml#.WCTymi0rJtQ. [Accessed 10 11 2016].

[27] "Analysis of Cyanide (Total, Weak Acid Dissociable, and Free)," British Columbia Environmental Services Department, Victoria, 2017.

[28] A. International, "D 6696-05 Standard Guide for Understanding Cyanide Species," ASTM International, West Conshohocken, PA, 2005.

[29] E. Gail, S. Gos, R. Kulzer, J. Lorösch, A. Rubo and M. Sauer, Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH, 1990.

[30] J. Daintith, A Dictionary of Chemistry, Oxford: Oxford University Press, 2008.

[31] J. Marsden and I. House, "Chemistry of Gold Extraction," Ellis Horwood, West Sussex, 1992.

[32] "International Cyanide Management Code," International Cyanide Management Institute, [Online]. Available: http://www.cyanidecode.org/cyanide-facts/sample-analysis. [Accessed 23 12 2016].

[33] H. Aman, "Molecular Neuroscience and General Chemistry Notes," Chem 1180, 3 October 2010. [Online]. Available: http://chem1180.blogspot.com/2010/10/163-164-base-ionization-equilibria.html. [Accessed 1 10 2014].

[34] C. A. Fleming, "Hydrometallurgy of Precious Metals Recovery," *Hydrometallurgy,* pp. 127-137, 1992.

[35] P. Verhoeven, G. T. Hefter and P. M. May, "Dissociation Constant of Hydrogen Cyanide in Saline Solutions," *Minerals and Metallurgical Processing,* pp. 185-188, 1990.

[36] S. Zumdahl, Chemical Principles, Boston: Houghton Mifflin, 2009, p. 265.

[37] S. Zumdahl and S. Zumdahl, Chemistry, Belmont: Brooks Cole, 2008, p. 657.

[38] R. W. Barlett, Solution Mining: Leaching and Fluid Recovery of Materials, Netherlands: Phychology Press, 1998, p. 60.

[39] M. Adams, "The Chemical Behaviour of Cyanide in the Extraction of Gold. 1. Kinetics of Cyanide Loss in the Presence and Absebce of Activated Carbon," *J.S. Afr. Inst. Min. Metall.,* vol. 90, no. 2, pp. 37-44, Feb. 1990.

[40] K. Osseo-Asare, T. Xue and V. S. T. Ciminelli, "Solution Chemistry of Cyanide Leaching Systems," *Precios Metals: Mining Extraction and Processing,* pp. 173-197, 1984.

[41] R. G. Luthy, "Kinetics of Reaction of Cyanide and Reduced Sulfur Species in Aqueous Solution," *Environmental Science & Technology,* vol. 13, no. 12, pp. 1481-1487, 1979.

[42] C. M. Flynn, S. L. Mc Gill, K. P. V. Lei and T. G. Carnahan, Chemistry of Cyanide, Derived and Related Species and Metal Cyanide Complexes in Leaching and Closure Operations, Butte, MT: US Bureau of Mines Information Circular, 1988.

[43] "Method OIA-1677-09 Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry, EPA-821-R-99-013," U.S. Environmental Protection Agency, Washington, D.C., 1999.

[44] "D 7572-11a Standard Guide for Recovery of Aqueous Cyanides by Extraction from Mine Rock and Soil," ASTM International, West Conshohocken, PA, 2015.

[45] "D 2036-09 Standard Test Methods for Cyanides in Water," ASTM International, West Conshohocken, PA, 2015.

[46] "D 7511-09e2 Determination of Total Cyanide by Segmented Flow Injection/On-Line UV Digestion-Gas Diffusionwith Amperometric Detection," ASTM International, West Conshohocken, PA, 2015.

[47] "D 7728-11 Standard Guide for Selection of ASTM Analytical Methods for Implementation of International Cyanide Management Code Guidance," ASTM International, West Conshohocken, PA, 2015.

[48] "D 7237-10 Standard Test Method for Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection," ASTM International, West Conshohocken, PA, 2015.

[49] "D 7284-08 New Standard Test Method for Total Cyanide in Water by Midi or Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection," ASTM International, West Conshohocken, PA, 2014.

[50] "ISO-14403:2002 Water Quality Determination of Total Cyanide and Free Cyanide by Continuous Flow Analysis," International Organization for Standardization, Geneva, Switzerland, 2012.

[51] B. Giudice, B. Jorgenson and M. Bryan, "Problems Associated with Using Current EPA Approved Total Cyanide Analytical Methods for Determining

Municipal Wastewater Treatment Plant NPDES Permit Compliance," Robertson-Bryan Inc, Elk Grove, CA, 2009.

[52] D. J. Vaughan, Mineral Chemistry of the Metallic Sulfides, Cambridge, England: Cambridge University Press, 1977.

[53] N. Hedley, Chemistry of Cyanidation, New York: American Cyanamid Co., 1958.

[54] G. Deschenes, A. Pratt, P. Riveros and M. Fulton, "Reactions of Gold and Sulfide Minerals," *Minerals and Metallurgical Process Journal,* vol. 19, no. 4, pp. 169-177, 2002.

[55] H. Guo, G. Deschenes, A. Pratt, M. Fulton and R. Lastra, "Leaching Kinetics and Mechanisms of Surface Reactions During Cyanidation of Gold in Presence of Pyrite and Stibnite," in *Annual SME Meeting 2004. Preprint 04-73*, Littleton, 2004.

[56] J. Li, S. Safarzadeh, M. Moats, J. Miller, M. LeVier, M. Dietrich and R. Wan, "Thiocyanate Hydrometallurgy for the Recovery of Gold. Part I: Chemical and Thermodynamic Considerations," *Hydrometallurgy,* vol. 113, no. 2012, pp. 1-9, 2012.

[57] E. Milosavljevic, "Reduced Sulfur Species in Cyanidation Effluents," Reno, Nevada, 2011.

[58] R. G. Luthy and S. G. Bruce, "Kinetics of Reaction of Cyanide and Reduced Sulfur Species in Aqueous Solution," *Environmental Science and Technology,* vol. 13, no. 12, pp. 1480-1488, 1979.

[59] W. H. Hill, "Recovery of Ammonia, Cyanogen, Pyridine and other Nitrogenous Compounds from Industrial Gases," *Chemistry of Coal Utilization,* vol. 2, 1945.

[60] R. Luthy, S. Bruce, R. Walters and D. Nakles, "Cyanide and Thiocyanate in Coal Gasification Wastewaters," *Water Pollution Control Federation,* vol. 51, no. 9, pp. 2267-2282, 1979.

[61] P. D. Barlett and R. E. Davis, "Reactions of Elemental Sulfur II. The Reaction of Alkali Cyanides and Some Single Sulfur Transfer Reactions," *Journal of the American Chemical Society,* vol. 80, no. 12, p. 2513, 1958.

[62] A. Roy and P. Trudinger, The Biochemistry of Inorganic Compounds of Sulphur, Cambridge: Cambridge university press, 1970.

[63] T. Austad, "Polythionates. I. The Reaction Between the Tetrathionate Ion and the Cyanide Ion in Acetonitrite," *Acta Chemica Scandinavica,* vol. 28, no. 1974, pp. 693-702, 1974.

[64] E. N. Wiberg and A. Holleman, Inorganic Chemistry, 1st ed. 2001., San Diego: Academic Press, 2001.

[65] A. Roy and P. Trudinger, The Biochemistry of Inorganic Compounds of Sulphur, Cambridge: University press, 1970.

[66] D. Lyons and G. Nickless, Inorganic Sulphur Chemistry, New York: Elsevier Publishing Company, 1968.

[67] C. O. Moses, D. K. Nordstrom, J. S. Herman and A. L. Mills, "Aqueous Pyrite Oxidation by Dissolved Oxygen and by Ferric Iron," *Geochimica et Cosmochimica Acta,* vol. 51, pp. 1561 - 1571, 1987.

[68] D. M. Muir and M. G. Aylmore, "Thiosulphate as an Alternative to Cyanide for Gold Processing – Issues and Impediments," *Mineral Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C),* vol. 113, no. 4, pp. C2 - C10, 2004.

[69] C. Moses, D. K. Nordstrom, J. Herman and A. Mills, "Aqueous Pyrite Oxidation by Dissolved Oxygen and by Ferric Iron," *Geochimica et Cosmochimica Acta,* vol. 51, no. 6, pp. 1561 - 1571, 1987.

[70] G. Nickless, Inorganic Sulfur Chemistry, New York: Elsevier, 1968.

[71] M. Aylmore and D. M. Muir, "Thiosulfate Leaching of Gold-A Review," *Mineral Engineering,* vol. 14, no. 2, pp. 135-174, 2001.

[72] J. A. Byerley and S. A. R. G. L. Fouda, "Kinetics and Mechanism of the Oxidation of Thiosulfate Ions by Copper(II) Ions in Aqueous Ammonia Solution," *J. Chem. Soc, Dalton Trans.,* pp. 889-893, 1973.

[73] C. Nicol and P. Fleming, "The Chemistry of the Extraction of Gold," in *The Extractive Metallurgy of Gold in South Africa*, Johannesburg, SAIMM, 1987, p. 831–905.

[74] H. Kellog and V. Kudryk, "Mechanism and Rate-Controlling Factors in the Dissolution of Gold in Cyanide Solution," *Journal of Metals,* vol. 3, no. 2, pp. 540-548, 1954.

[75] L. Elsner, "Über Das Verhalten Verschiedener Metale in Einer Wassrigen lössung von Zyankalium," *J. Prakt. Chem. 37,* pp. 441 - 446, 1846.

[76] G. Senanayake, "Kinetics and Reaction Mechanism of Gold Cyanidation: Surface Reaction Model via Au(I)-OH-CN Complexes," *Hydrometallurgy,* vol. 80, no. 1-2, pp. 1-12, 2005.

[77] M. E. Wadsworth, "Gold Dissolution and Activation in Cyanide Solution," *Hydrometallurgy,* vol. 57, no. 1, pp. 1-11, 2000.

[78] G. Senanayake, "Gold Leaching in Non-Cyanide Lixiviant Systems: Critical Issues on Fundamentals and Applications," *Minerals Engineering,* vol. 17, no. 2004, pp. 785-801, 2004.

[79] G. Deitz and J. Halpern, "Reaction of Silver with Aqueous Solutions of Cyanide and Oxygen. J. Met. 1109–1116," *Journal of Metals,* pp. 1109-1116, 1954.

[80] B. Johnson and R. Davis, Comprehensive Inorganic Chemistry Vol 5, Elmsford, NY: Pergamon Press, 1973.

[81] H. White, "The Solubility of Gold in Thiosulfates and Thiocyanates, , 1905, 5 109-111.," *Journal of the Chemical Metallurgical and Mining Society of South Africa,* vol. 5, no. 1, pp. 109-111, 1905.

[82] G. L. R Luna, "Cyanidation Kinetics of Silver Sulfide," *Hydrometallurgy,* vol. 56, no. 20000, p. 171–188, 2000.

[83] G. Senanayake, "The Cyanidation of Silver Metal: Review of Kinetics and Reaction Mechanism," *Hydrometallurgy,* vol. 81, pp. 75-85, 2006.

[84] V. Kudryk and H. H. Kellog, "Mechanism and Rate Cotrolling Factors in the Dissoltion of Gold in Cyanide Solution," *Journal of Metals,* vol. 6, pp. 541-548, 1954.

[85] M. Kameda, "Fundemental Studies on Solution of Gold in Cyanide Solutions, Effects of Alkalines, Lead Acetate and some Impurities contained in Foul," The Research Instiute of Mineral Dressing and Metallurgy, 1949.

[86] L. R. P. de Andrade Lima and D. Hodouin, "A Lumped Kinetic Model for Gold Ore Cyanidation," *Hydrometallurgy,* vol. 79, pp. 121-137, 2005.

[87] P. Kondos, G. Deschenes and G. Morrison, "Process Optimization Studies in Gold Cyanidation," *Hydrometallurgy,* pp. 235-250, 1995.

[88] F. Habashi, Principles of Extractive Metallurgy. Hydrometallurgy vol. 2., New York: Gordon and Breach, 1970.

[89] L. Lorenzen and J. S. J. van Deventer, "Electrochemical Interactions Between Gold and its Associated Minerals during Cyanidation," *Hydrometallurgy 30,* pp. 177-194, 1992.

[90] J. Li, T. K. Zhong and M. E. Wadsworth, "Application of mixed potential theory in hydrometallurgy," *Hydrometallurgy 30,* pp. 47 - 60, 1992.

[91] F. K. Crundwell and S. A. Godorr, "A Mathematical Model of the Leaching of Gold in Cyanide Solutions," *Hydrometallurgy,* vol. 44, pp. 147 -162, 1997.

[92] G. G. Schlessinger, Inorganic Laboratory Preparations, New York: Chemical Publishing Company, 1962, pp. 70-71.

[93] S. S. Zumdahl and D. J. DeCoste, Basic Chemistry, Stamford: Cengage Learning, 2011, p. 136.

[94] A. M. Comey, A Dictionary of Chemical Solubilities, New York: The Macmillian Company, 1921.

[95] J.T.Baker, "Sodium Hydroxide Baker Analyzed Reagent Pellets, Low in Carbonate," Avantor Performance Materials, Center Valley, 2011.

[96] S. S. Zumdahl and D. J. DeCoste, Basic Chemistry, Stamford: Cengage Learning, 2011, p. 217.

[97] Graymont, "High Calcium Quicklime Material Safety Data Sheet," Salt Lake City, 2014.

[98] SigmaAldrich, "Sodium Cyanide," 14 September 2014. [Online]. Available: http://www.sigmaaldrich.com/catalog/product/sial/380970?lang=en&region=US.

[99] Z. M. Abouzeid, Mineral Processing Laboratory Manual, Clausthal: Trans Tech Publications, 1990, pp. 11-23.

[100] E. E. Bugbee, A Textbook of Fire Assaying, London: John Wiley & Sons Inc., 1922.

[101] O. C. Shepard and W. F. Dietrich, Fire Assaying, New York: McGraw-Hill, 1940.

[102] "Fire Assaying: An Overview," Reno, 2007.

[103] O. Analytical, "Cyanide Analysis Guide," OI Analytical, College Station, Texas, 2010.

[104] M. A. Farrukh, Atomic Absorption Spectrometry (AAS), Mexico City: InTEch, 2012.

[105] R. F. Lee, "Simultaneous Determination of Carbon and Sulphur in Geological Material Using Inductive Combustion," *Chemical Geology,* vol. 31, pp. 145-151, 1980.

[106] "Cyanolysis and Spectrophotometric Estimation of Trithionate in Mixture with Thiosulfate and Tetrathionate," *Analytical Chemistry,* vol. 41, no. 7, pp. 898-901, 1969.

[107] E. Hogfeldt, "Stability Constants of Metal-Ion Complexes, 2nd Supplement," in *IUPAC Chemical data series No. 2, part A, Inorganic ligands*, Oxford, Pergamon, 1982.

[108] A. G. Sharpe, The Chemistry of Cyano Complexes of the Transition Metals, New York: Academic Press City, 1976.

[109] T. M. Subzhiyeva and I. Volkov, "Thiosulphates and sulphites in thermal and hydrothermal waters," *Geo-chem. Int.,* vol. 19, no. 4, pp. 94-98, 1982.

[110] G. Senanayake, "Gold Leaching by Thiosulphate Solutions: A Critical Review on Copper(II)–Thiosulphate–Oxygen Interactions," *Minerals Engineering,* vol. 18, pp. 995-1006, 2005.

[111] W. N. Perera, G. Senanayake and M. J. Nicol, "Interaction of Gold(I) with Thiosulfate–Sulfite Mixed Ligand Systems.," *Inorganica Chimica Acta,* vol. 358, no. 7, p. 2183–2190, 2005.

[112] J. G. Webster, "The Solubility of Gold and Silver in the System Au-Ag-S-O2-H2O at 25 C and 1 atm," *Geochemica en Cosmochimica Acta,* vol. 50, pp. 1837-1845, 1986.

[113] D. Feng and J. S. J. Deventer, "Effect of Sulfides on Gold Dissolution in Ammoniacal Thiosulfate Medium," *Metallurgical and Materials Transactions,* vol. 34B, pp. 5-13, 2003.

[114] K. Tozawa, Y. Iniu and Y. Umetsu, "Dissolution of Gold in Ammonical Thiosulphate Solutions," in *Annual AIME Meeting*, 1981.

[115] K. A. Ter-Arakelyan, "On technological expediency of sodium thiosulphate usage for gold extraction from raw material," *Izv. V.U.Z. Tsvetn. Metallurgy,* pp. 72-76, 1984.

[116] H. G. Zhang and D. B. Dreisinger, "The Kinetics for the Decomposition of Tetrathionate in Alkaline Solutions," *Hydrometallurgy,* vol. 66, pp. 59-65, 2002.

[117] M. I. Jeffrey, "Kinetic aspects of gold and silver leaching in ammonia–thiosulfate solutions," *Hydrometallurgy,* vol. 60, pp. 7-16, 2001.

APPENDIX A: EXPERIMENTAL CONDITIONS AND DATA

Exp#	Bottle (g)	Bottle + solid (g)	Bottle + solid + water (g)
BR7	1,016.0	1,320.5	1,620.5
BR8	1,014.0	1,318.5	1,618.5
BR9	1,015.5	1,319.0	1,619.0
BR10	1,030.5	1,335.0	1,635.0
BR11	1,014.0	1,318.0	1,618.0
BR27	1,012.0	1,313.0	1,617.0
BR28	1,025.0	1,326.5	1,629.0
BR29	1,014.5	1,315.0	1,614.5
BR30	1,014.5	1,320.0	1,621.5
BR31	1,012.5	1,322.0	1,622.5
BR42	1,025.5	1,327.0	1,639.0
BR18	1,013.0	1,314.5	1,612.5
BR19	1,014.5	1,316.5	1,619.0
BR20	1,012.0	1,313.0	1,609.5
BR21	1,014.0	1,316.5	1,618.5
BR22	1,025.5	1,328.0	1,627.5
BR23	1,014.5	1,317.0	1,619.0
BR24	1,013.0	1,316.5	1,617.0
BR25	1,013.0	1,315.5	1,617.0
BR26	1,015.0	1,317.5	1,623.5
BR45	1,012.5	1,315.5	1,621.0
BR33	1,014.5	1,318.0	1,623.0
BR34	1,025.5	1,331.0	1,631.0
BR35	1,012.5	1,313.5	1,620.0
BR36	1,014.0	1,319.0	1,624.0
BR37	1,028.0	1,331.5	1,631.5
BR38	1,012.0	1,313.0	1,613.0
BR39	1,012.0	1,312.0	1,612.0
BR40	1,014.0	1,315.5	1,615.5

Table 47. Bottle Weight Measurements

Exp#	NaCN lb/st sample	Initial target NaCN (ppm)	Initial target $S_4O_6^{2-}$ (ppm)	Initial target SO_3^{2-} (ppm)	Added $Na_2S_4O_6.2H_2O$ (g)	Added 10,000 ppm SO_3^{2-} (ml)	Added NaCN (g)	Added $Ca(OH)_2$ (g)
BR1	0.50	250	0	0	0.000	0.0	0.075	1.74
BR7	1.00	500	0	0	0.000	0.0	0.150	1.50
BR8	1.00	500	300	0	0.123	0.0	0.150	1.50
BR9	1.00	500	300	100	0.123	3.0	0.150	1.50
BR10	1.00	500	300	200	0.123	6.0	0.150	1.50
BR11	1.00	500	300	300	0.123	9.0	0.150	1.50
BR27	1.00	500	0	0	0.000	0.0	0.150	1.50
BR28	1.00	500	300	0	0.123	0.0	0.150	1.50
BR29	1.00	500	300	100	0.123	3.0	0.150	1.50
BR30	1.00	500	300	200	0.123	6.0	0.150	1.50
BR31	1.00	500	300	300	0.123	9.0	0.150	1.50
BR42	1.50	750	0	0	0.000	0.0	0.225	1.50
BR18	1.50	750	300	0	0.123	0.0	0.225	1.50
BR19	1.50	750	300	100	0.123	3.0	0.225	1.50
BR20	1.50	750	300	200	0.123	6.0	0.225	1.50
BR21	1.50	750	300	300	0.123	9.0	0.225	1.50
BR22	1.50	750	0	0	0.000	0.0	0.225	1.50
BR23	1.50	750	300	0	0.123	0.0	0.225	1.50
BR24	1.50	750	300	100	0.123	3.0	0.225	1.50
BR25	1.50	750	300	200	0.123	6.0	0.225	1.50
BR26	1.50	750	300	300	0.123	9.0	0.225	1.50
BR45	2.00	1000	0	0	0.000	0.0	0.300	1.50
BR33	2.00	1000	300	0	0.123	0.0	0.300	1.50
BR34	2.00	1000	300	100	0.123	3.0	0.300	1.50
BR35	2.00	1000	300	200	0.123	6.0	0.300	1.50
BR36	2.00	1000	300	300	0.123	9.0	0.300	1.50
BR37	2.00	1000	0	0	0.000	0.0	0.300	1.50
BR38	2.00	1000	300	0	0.123	0.0	0.300	1.50
BR39	2.00	1000	300	100	0.123	3.0	0.300	1.50
BR40	2.00	1000	300	200	0.123	6.0	0.300	1.50
BR41	2.00	1000	300	300	0.123	9.0	0.300	1.50

Table 48. Experiment Reagent Amounts

Exp#	Au in solution (mg/L)	Ag in solution (mg/L)	Cu in solution (mg/L)	Au in tailings (oz/st)	AuCN in tailings (oz/st)	Ag in tailings (oz/st)	Cu in tailings (%)	Calc. Au head (oz/st)	Calc. Ag head (oz/st)	Calc. Cu head (%)	Account. Au (%)	Account. Ag (%)	Account. Cu (%)
BR7	0.31	0.31	1.85	0.1895	0.0257	2.975	2.04	0.2111	2.9841	2.04	108.1	98.7	101.1
BR8	0.74	0.41	2.79	0.1863	0.0280	2.958	1.99	0.2090	2.9700	1.99	107.0	98.3	98.7
BR9	0.78	0.42	3.27	0.1899	0.0251	2.946	1.97	0.2153	2.9583	1.97	110.2	97.9	97.7
BR10	0.87	0.46	3.31	0.1853	0.0257	3.022	2.1	0.2086	3.0354	2.10	106.8	100.4	104.1
BR11	0.80	0.45	3.35	0.1874	0.0257	2.981	2.07	0.2131	2.9941	2.07	109.1	99.1	102.6
BR27	0.88	0.37	2.33	0.2071	0.0368	2.94	1.63	0.2310	2.9508	1.63	118.3	97.6	80.8
BR28	0.82	0.42	2.84	0.2321	0.0368	2.999	1.79	0.2555	3.0113	1.79	130.8	99.6	88.8
BR29	0.80	0.38	2.25	0.1897	0.0362	2.952	1.86	0.2134	2.9631	1.86	109.2	98.1	92.2
BR30	0.81	0.49	3.79	0.2241	0.0344	2.97	1.73	0.2530	2.9843	1.73	129.5	98.8	85.8
BR31	0.99	0.47	3.68	0.2021	0.0356	2.94	1.79	0.2278	2.9537	1.79	116.6	97.7	88.8
BR42	0.88	0.29	6.56	0.2101	0.0251	2.929	1.7	0.2428	2.9375	1.71	124.3	97.2	84.5
BR18	1.12	0.34	18.65	0.1981	0.0286	2.911	1.93	0.2317	2.9209	1.95	118.6	96.7	96.5
BR19	1.15	0.36	13.45	0.1899	0.028	2.864	1.92	0.2211	2.8745	1.93	113.2	95.1	95.7
BR20	1.07	0.35	15.60	0.1966	0.0274	2.812	1.85	0.2302	2.8222	1.87	117.8	93.4	92.4
BR21	1.15	0.41	17.05	0.1855	0.0292	2.905	1.92	0.2176	2.9170	1.94	111.4	96.5	95.9
BR22	1.10	0.34	15.45	0.1995	0.0286	2.847	1.76	0.2375	2.8569	1.78	121.6	94.5	87.9
BR23	1.30	0.41	22.20	0.1873	0.0216	2.829	1.79	0.2258	2.8410	1.81	115.6	94.0	89.7
BR24	1.32	0.45	21.60	0.1687	0.0216	3.01	1.83	0.2075	3.0231	1.85	106.2	100.0	91.7
BR25	1.33	0.44	28.55	0.1989	0.0228	2.987	1.71	0.2383	2.9998	1.74	122.0	99.3	86.1
BR26	1.35	0.49	31.80	0.1783	0.021	2.899	1.78	0.2168	2.9133	1.81	111.0	96.4	89.7
BR45	1.32	0.26	20.50	0.1813	0.0257	3.285	1.75	0.2175	3.2926	1.77	111.4	109.0	87.6
BR33	1.24	0.41	75.90	0.2151	0.0239	2.853	1.75	0.2554	2.8650	1.83	130.8	94.8	90.4
BR34	1.38	0.45	63.20	0.2041	0.0222	2.864	1.81	0.2470	2.8771	1.87	126.5	95.2	92.7
BR35	1.47	0.43	92.40	0.1923	0.0239	2.835	1.82	0.2323	2.8476	1.91	118.9	94.2	94.7
BR36	1.37	0.46	81.90	0.1835	0.0239	2.829	1.74	0.2241	2.8424	1.82	114.7	94.1	90.2
BR37	1.39	0.30	34.20	0.1889	0.0263	2.899	1.67	0.2283	2.9078	1.70	116.9	96.2	84.4
BR38	1.35	0.39	47.20	0.1751	0.0245	2.841	1.58	0.2154	2.8524	1.63	110.3	94.4	80.6
BR39	1.38	0.49	53.50	0.1709	0.0245	2.824	1.65	0.2103	2.8383	1.70	107.7	93.9	84.3
BR40	1.35	0.50	61.60	0.1825	0.0251	2.894	1.67	0.2231	2.9086	1.73	114.2	96.2	85.7
BR41	1.39	0.63	76.90	0.1917	0.0263	2.859	1.69	0.2320	2.8774	1.77	118.8	95.2	87.5

Table 49. Calculated Head Assay Accountabilities

APPENDIX B: DUPLICATE EXPERIMENTS RESULTS

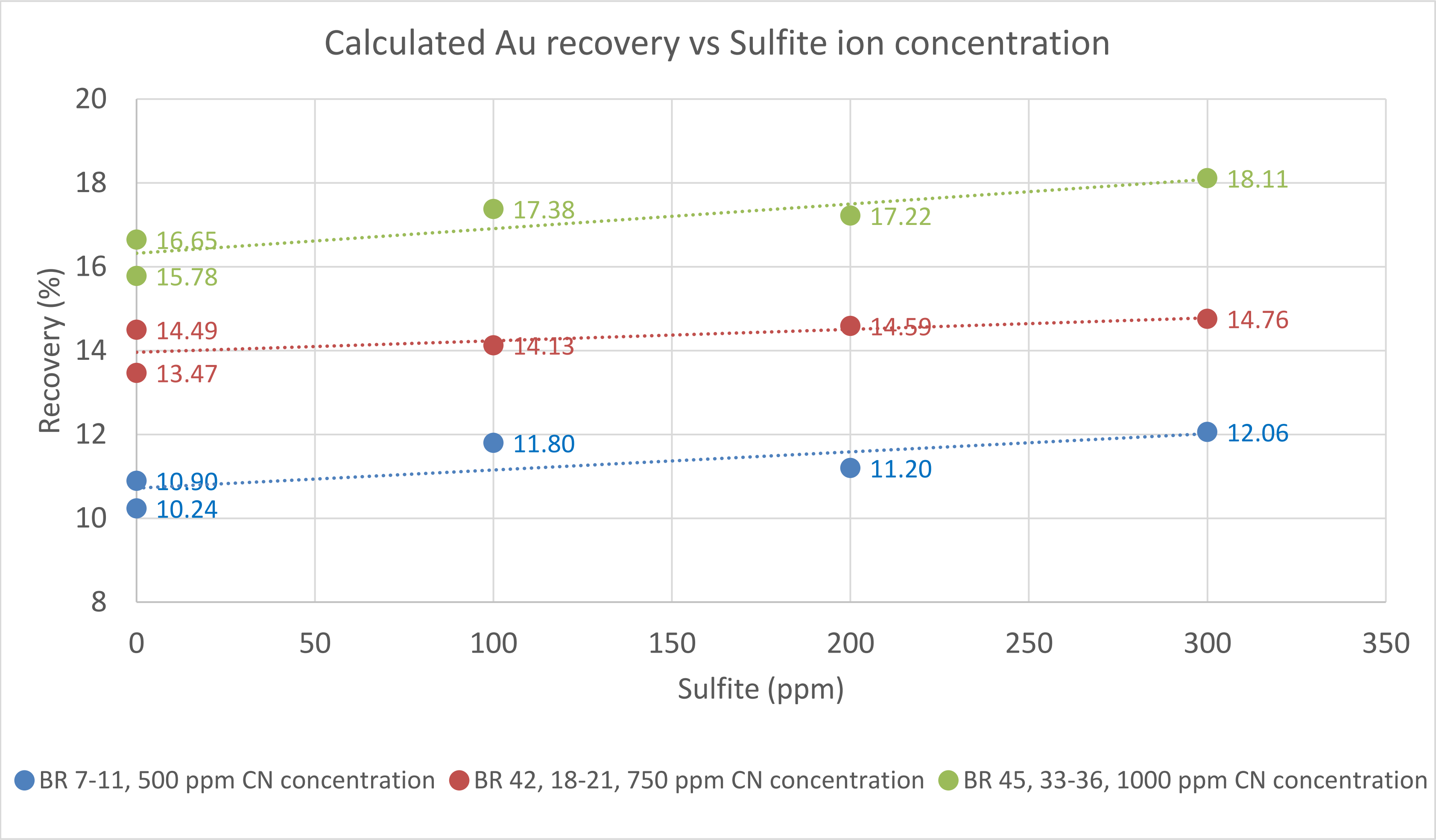


Figure 52. Calculated Au Recovery vs Sulfite Ion Concentration (Duplicates)

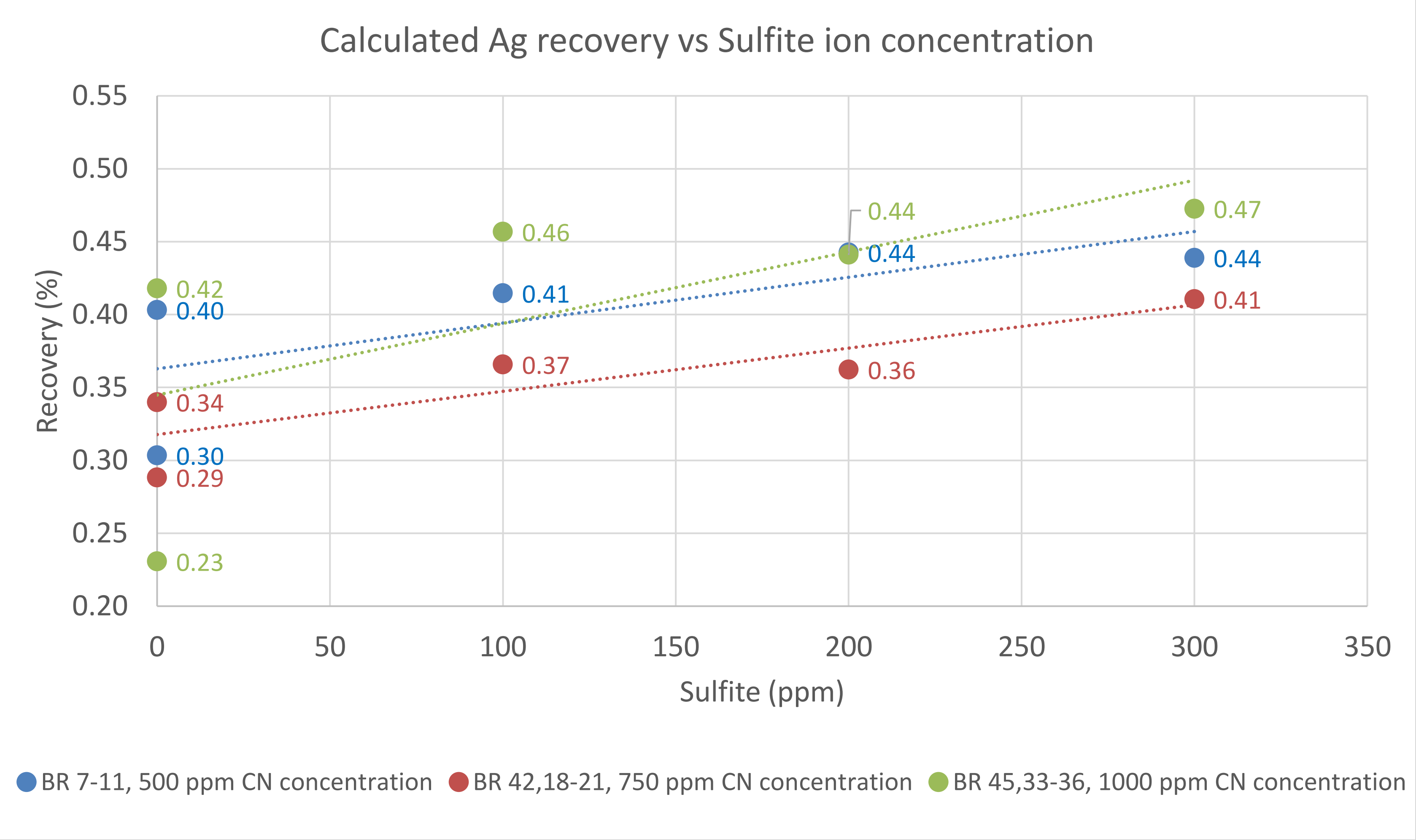


Figure 53. Calculated Ag Recovery vs Sulfite Ion Concentration (Duplicates)

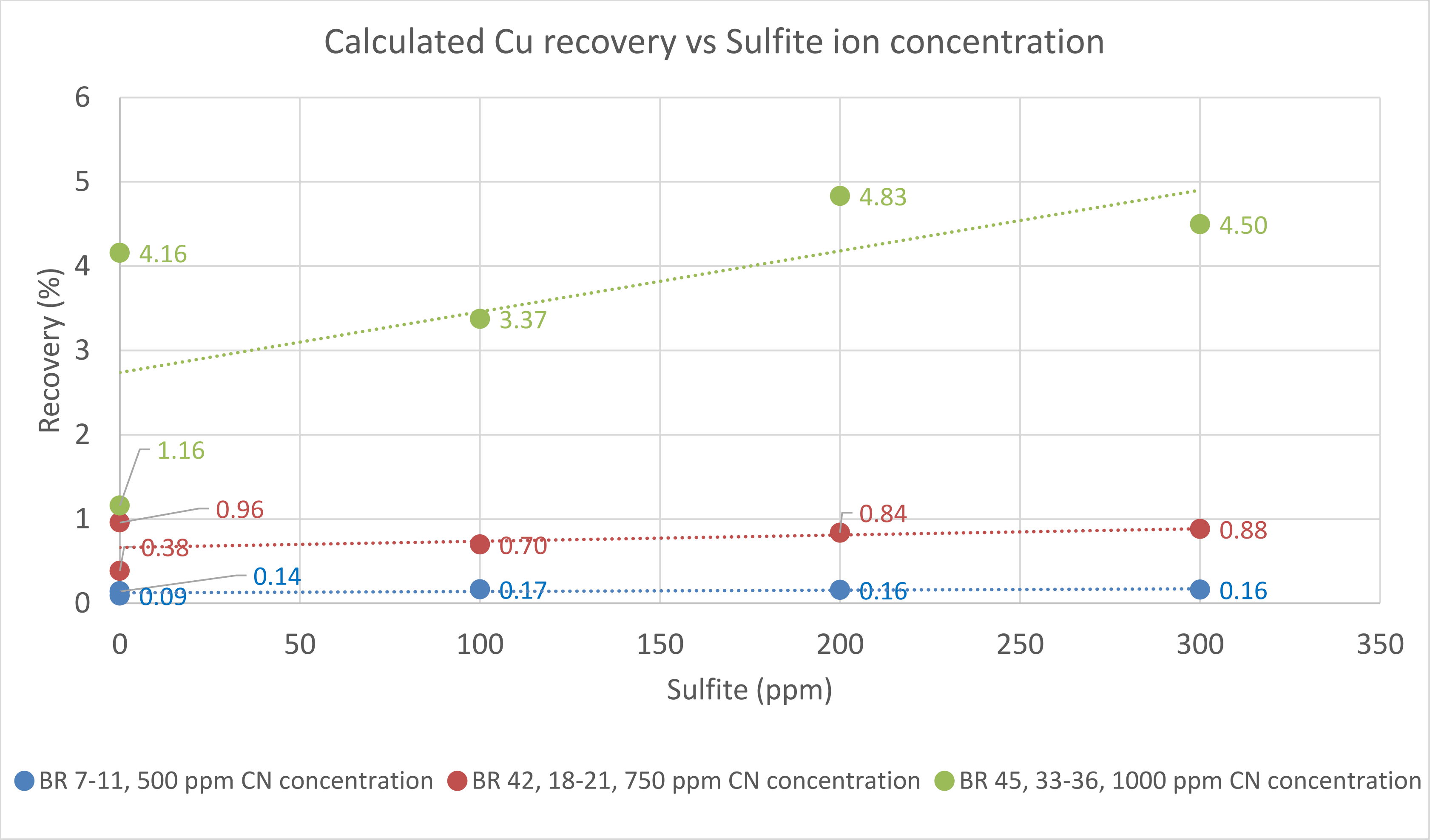


Figure 54. Calculated Cu Recovery vs Sulfite Ion Concentration (Duplicates)

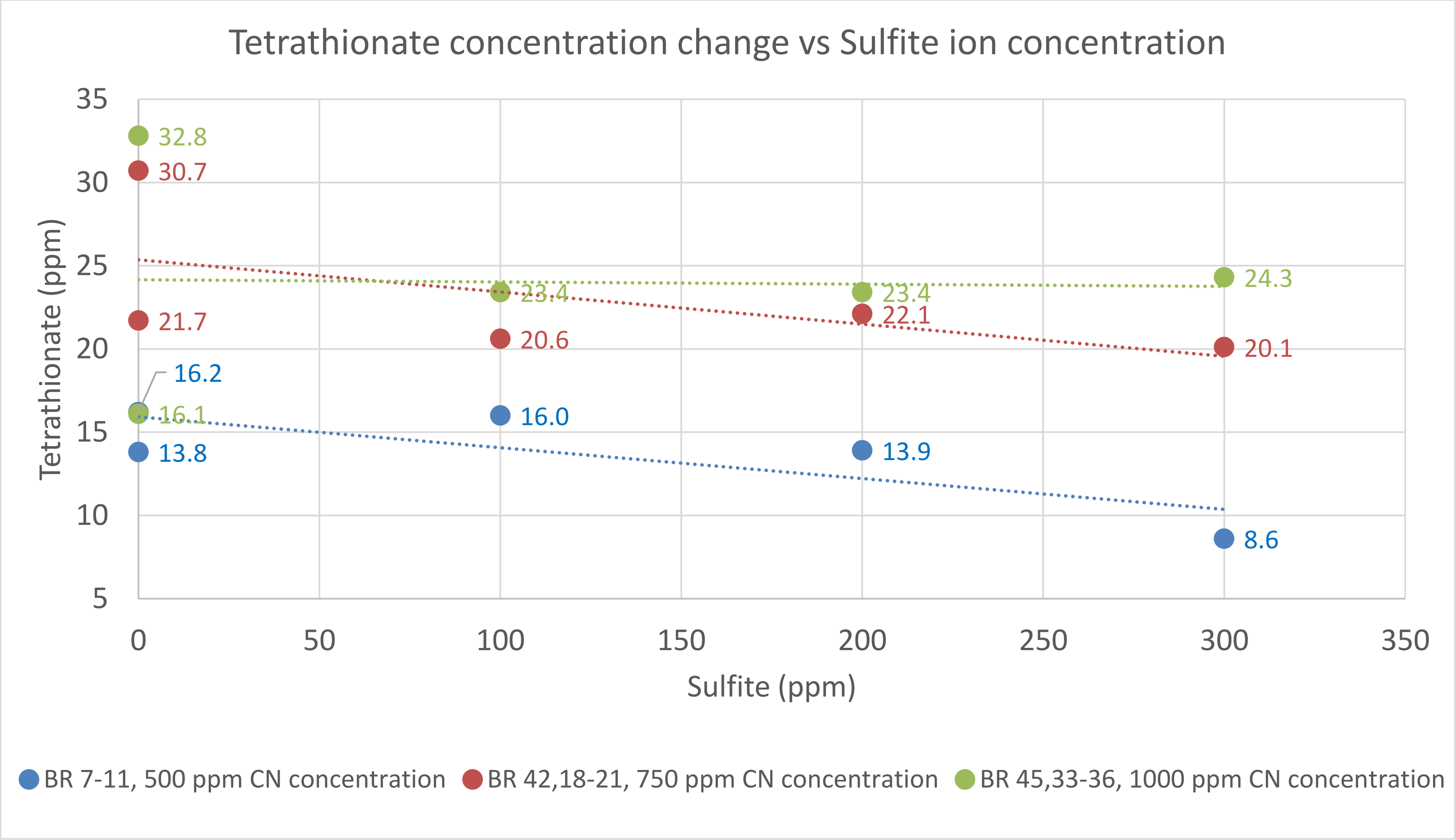


Figure 55. Tetrathionate Concentration Change vs Sulfite Ion Concentration (Duplicates)

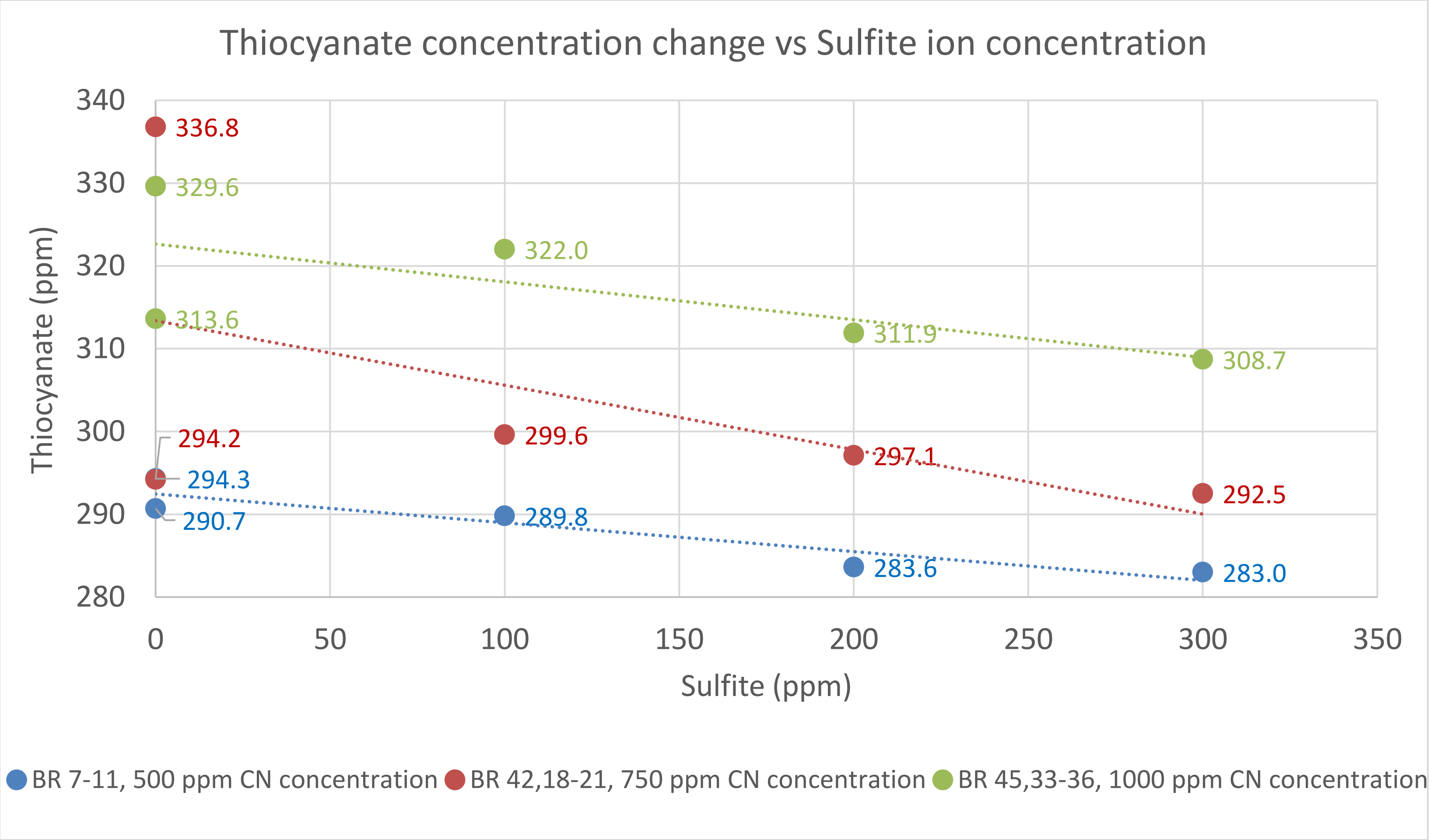


Figure 56. Thiocyanate concentration change vs Sulfite ion concentration (Duplicates)

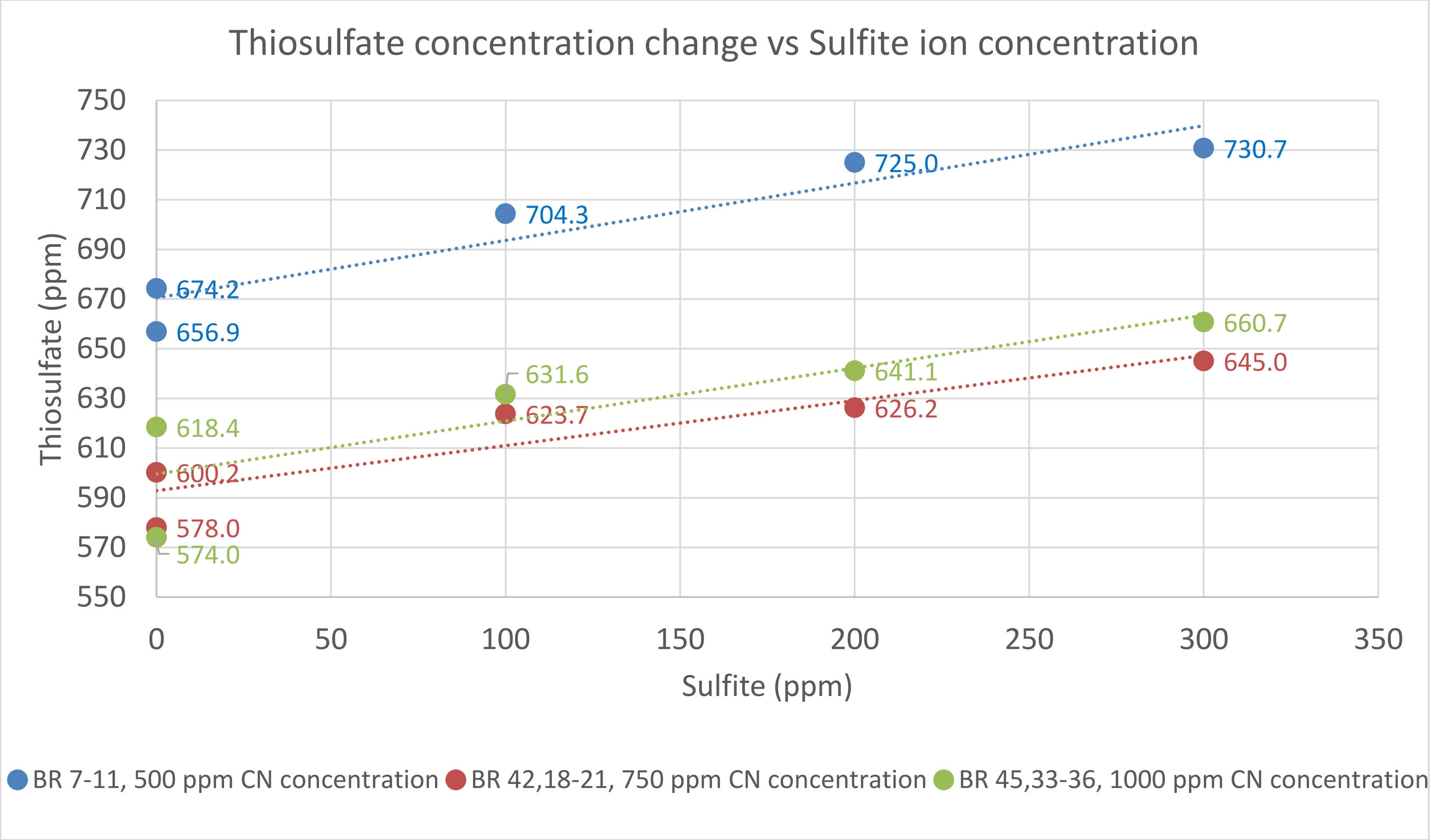


Figure 57. Thiosulfate Concentration Change vs Sulfite Ion Concentration (Duplicates)

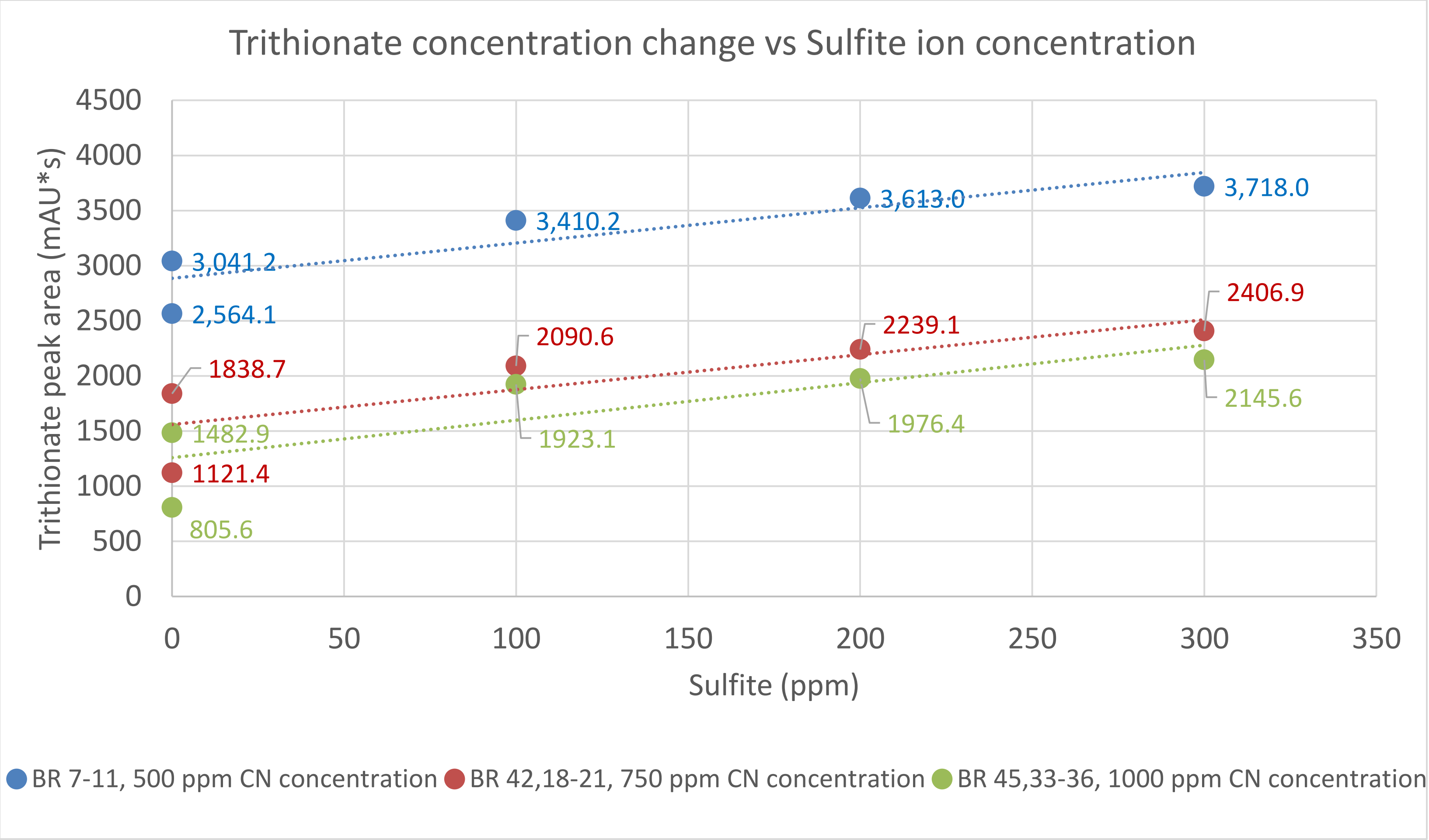
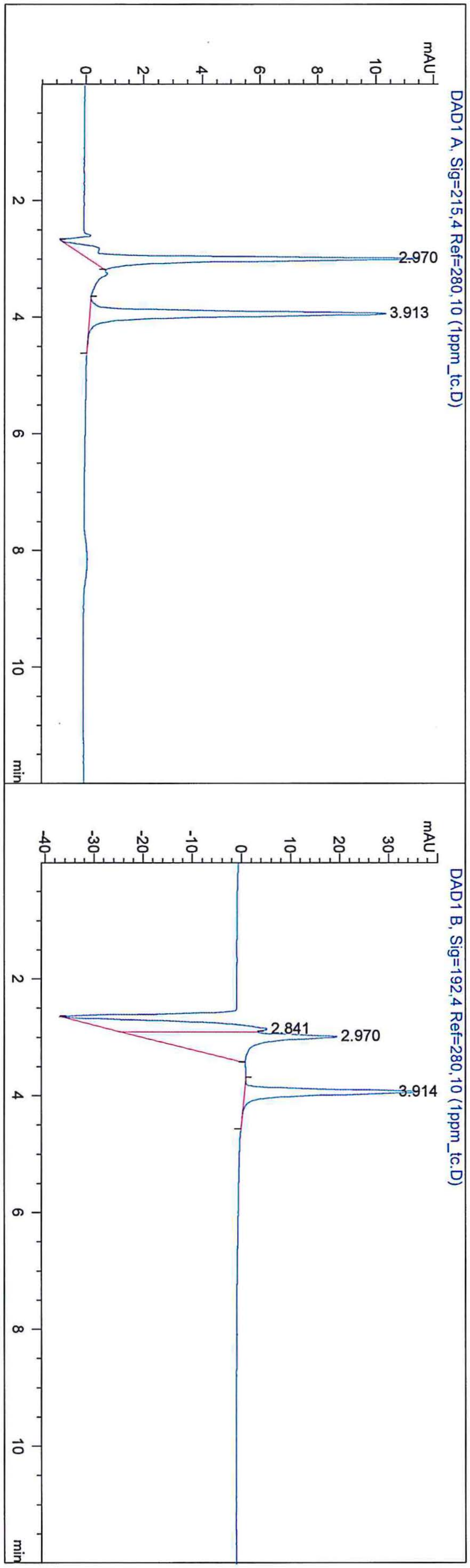


Figure 58. Trithionate Concentration Change vs Sulfite Ion Concentration (Duplicates)

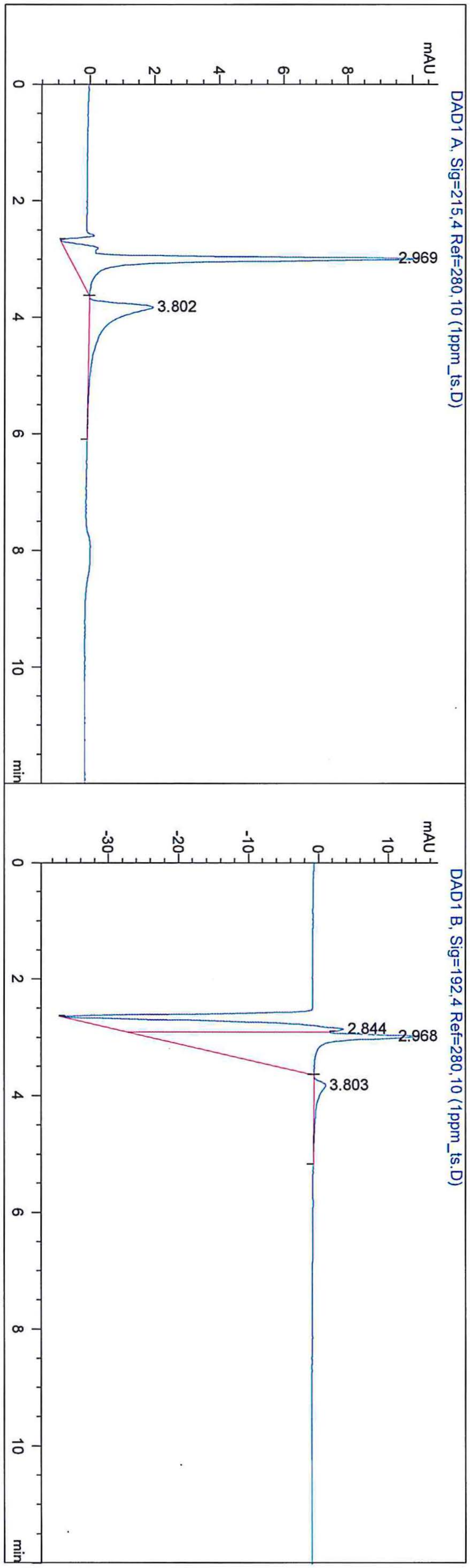
APPENDIX C: HPLC CALIBRATION PROFILE

```
=====================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   7
Acq. Instrument : Two Socks                        Location :   7
Injection Date  : 4/12/2017 1:51:02 PM                  Inj :   1
                                                Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```


DAD1 A, Sig=215,4 Ref=280,10 (1ppm_tc.D)
mAU
0
2
4
6
8
10
2.970
3.913
2
4
6
8
10
min
DAD1 B, Sig=192,4 Ref=280,10 (1ppm_tc.D)
mAU
-40
-30
-20
-10
0
10
20
30
2.841
2.970
3.914
2
4
6
8
10
min

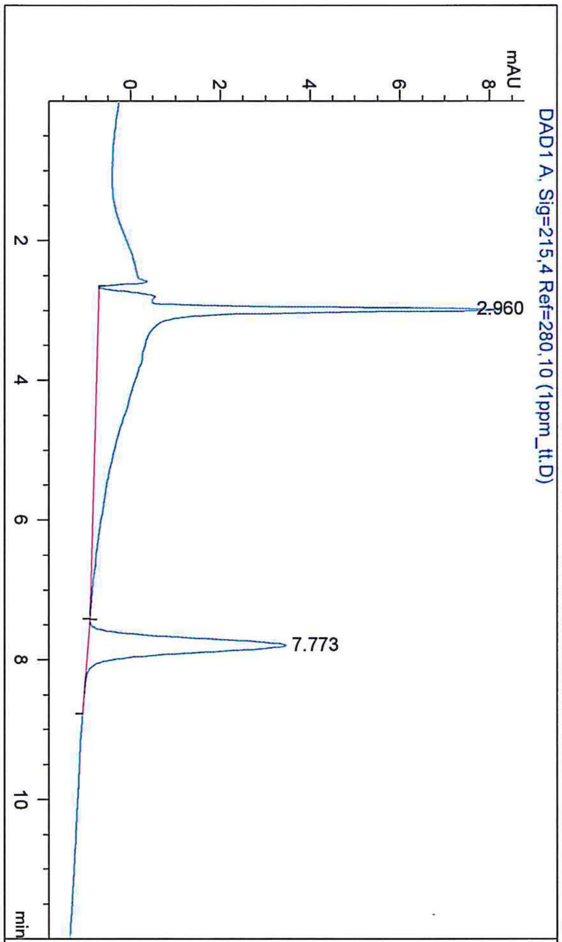
```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.970 BB    0.0925   73.73462   11.54873  50.5547
   2   3.913 BB    0.1064   72.11656   10.20659  49.4453

Totals :                   145.85118   21.75532



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.841 BV    0.1504  365.85315   32.23018  31.8454
   2   2.970 VB    0.1724  534.16736   40.36815  46.4962
   3   3.914 BB    0.1049  248.82050   35.88706  21.6584

Totals :                  1148.84100  108.48539


=====================================================================
                          *** End of Report ***
```

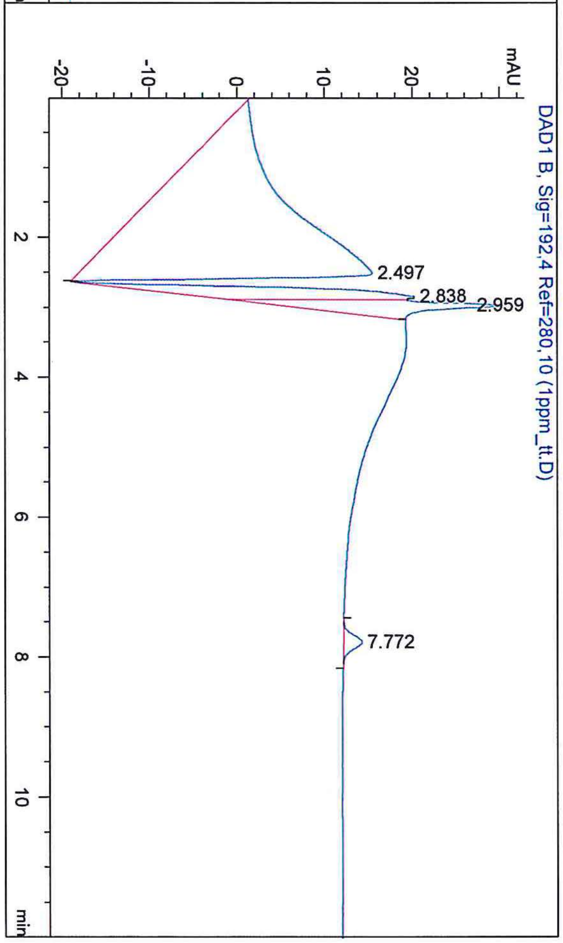
```
=====================================================================
Acq. Operator   : SYSTEM                         Seq. Line :   4
Acq. Instrument : Two Socks                       Location :   4
Injection Date  : 4/12/2017 1:07:46 PM                 Inj :   1
                                                Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```


DAD1 A, Sig=215,4 Ref=280,10 (1ppm_ts.D)
mAU
0
2
4
6
8
2.969
3.802
0
2
4
6
8
10
min
DAD1 B, Sig=192,4 Ref=280,10 (1ppm_ts.D)
mAU
-30
-20
-10
0
10
2.844
2.968
3.803
0
2
4
6
8
10
min

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.969 BB    0.1109   86.86102   10.90897  66.8272
   2   3.802 BB    0.2868   43.11752    2.00544  33.1728

Totals :                   129.97854   12.91441



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.844 BV    0.1521  376.74072   32.77720  34.3317
   2   2.968 VB    0.2220  684.86969   39.17080  62.4110
   3   3.803 BB    0.2767   35.74333    1.71828   3.2572

Totals :                  1097.35374   73.66628


=====================================================================
                          *** End of Report ***
```

```
    =====================================================================
    Acq. Operator   : SYSTEM                         Seq. Line :   1
    Acq. Instrument : Two Socks                       Location :   1
    Injection Date  : 4/12/2017 12:24:31 PM                Inj :   1
                                                    Inj Volume : 25.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
    Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
    Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                      Sequence Method)
    Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
    Method Info     : SULFUR SPECIES
```

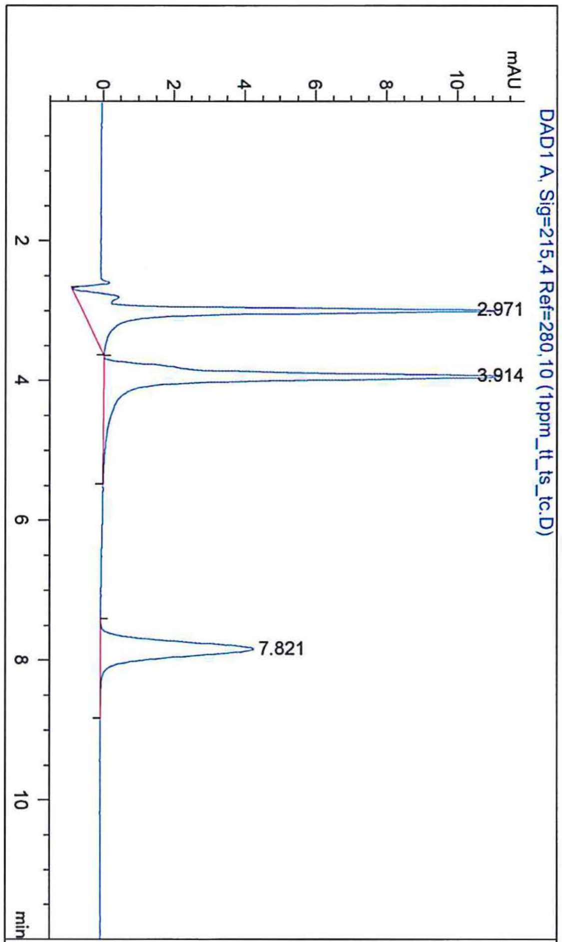

DAD1 A, Sig=215,4 Ref=280,10 (1ppm_tt.D)
mAU
0
2
4
6
8
2
4
6
8
10
min
2.960
7.773

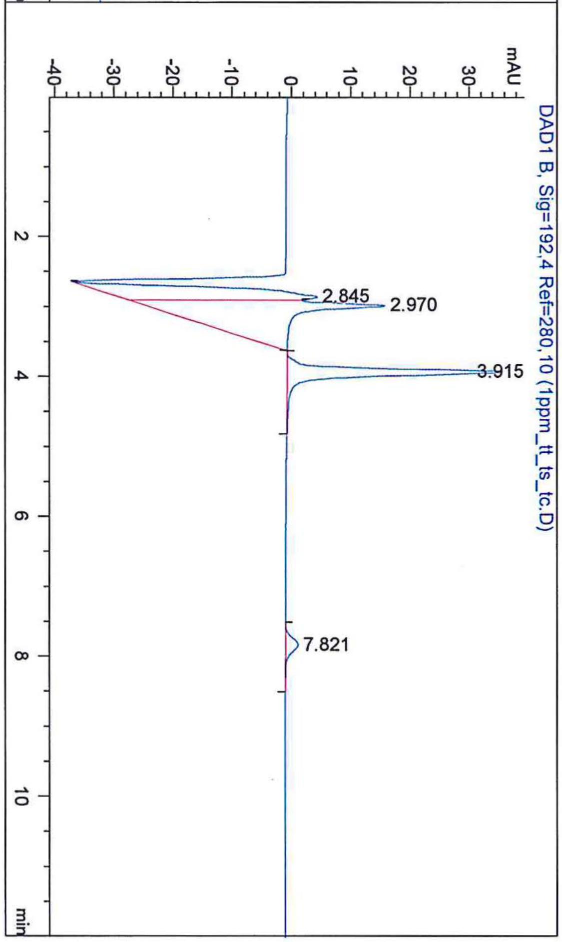

DAD1 B, Sig=192,4 Ref=280,10 (1ppm_tt.D)
mAU
-20
-10
0
10
20
2
4
6
8
10
min
2.497
2.838
2.959
7.772

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.960 BB    0.2670  192.93861    9.04171  74.7730
   2   7.773 BB    0.2257   65.09399    4.42217  25.2270

Totals :                   258.03261   13.46388



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.497 BB    0.8312 2290.63232   33.52162  80.3436
   2   2.838 BV    0.1585  296.14545   24.24874  10.3873
   3   2.959 VB    0.1234  233.21527   25.81115   8.1800
   4   7.772 BB    0.2272   31.05268    2.14061   1.0892

Totals :                  2851.04573   85.72212


=====================================================================
                          *** End of Report ***
```

```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  10
Acq. Instrument : Two Socks                      Location :   10
Injection Date  : 4/12/2017 2:34:19 PM                Inj :   1
                                               Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```

Data File C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\1ppm_tt_ts_tc.D
Sample Name: 1ppm_tt_ts_tc

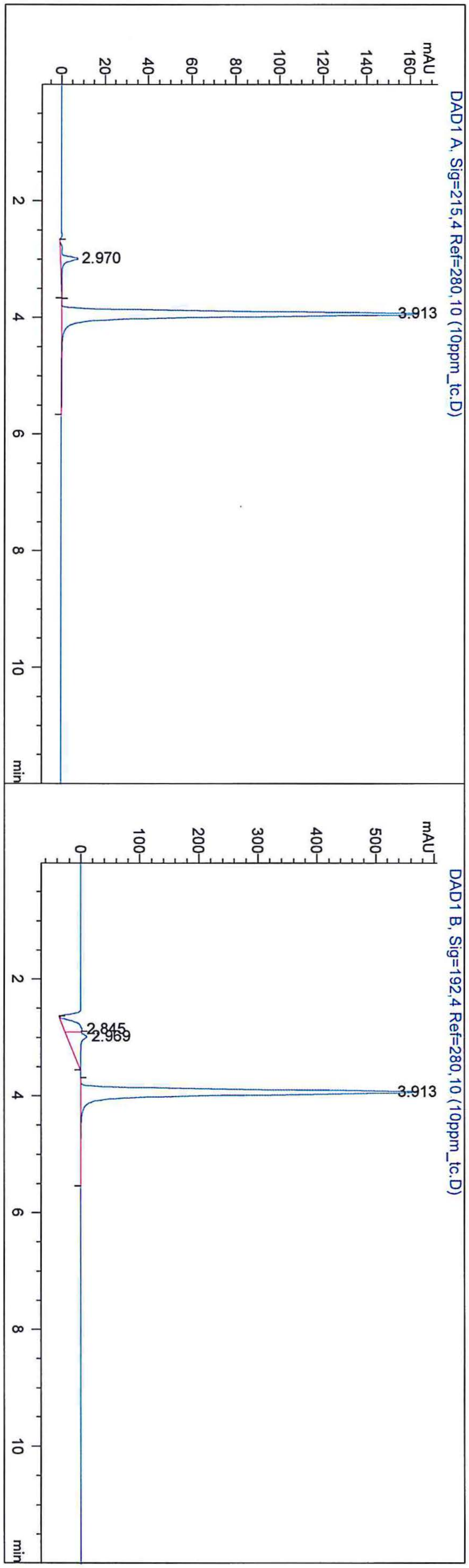




```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.971 BB    0.1103   93.30506   11.78809 34.7638
   2   3.914 BB    0.1389  110.99892   11.27249 41.3562
   3   7.821 BB    0.2269   64.09321    4.32577 23.8800

Totals :                   268.39719   27.38636



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.845 BV    0.1507  390.35190   33.80644 28.1111
   2   2.970 VB    0.2163  689.58716   40.57843 49.6605
   3   3.915 BB    0.1147  276.72681   36.41764 19.9284
   4   7.821 BB    0.2255   31.93626    2.17295  2.2999

Totals :                  1388.60213  112.97546


=====================================================================
                          *** End of Report ***
```

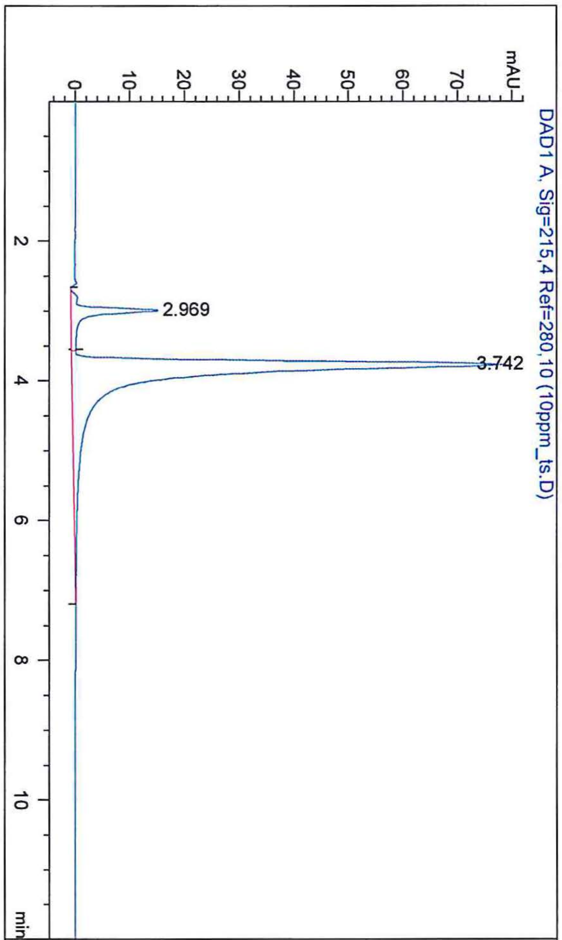
```
=====================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   8
Acq. Instrument : Two Socks                        Location :   8
Injection Date  : 4/12/2017 2:05:30 PM                  Inj :   1
                                                 Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```

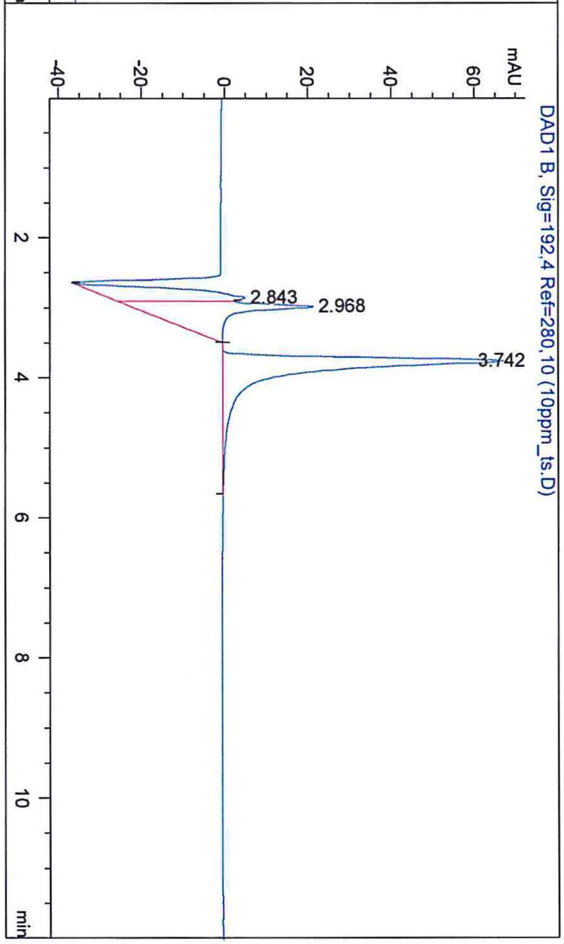
Data File C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\10ppm_tc.D
Sample Name: 10ppm_tc



```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.970 BB    0.1196   70.26507    8.06935   5.8239
   2   3.913 BB    0.1046 1136.23730  164.47090  94.1761

Totals :                  1206.50237  172.54025



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.845 BV    0.1567  366.84335   30.85996   7.4209
   2   2.969 VB    0.2189  589.04242   34.21471  11.9157
   3   3.913 BB    0.1049 3987.51001  574.75366  80.6634

Totals :                  4943.39578  639.82833


=====================================================================
                          *** End of Report ***
```

```
=====================================================================
Acq. Operator   : SYSTEM                         Seq. Line :   5
Acq. Instrument : Two Socks                       Location :   5
Injection Date  : 4/12/2017 1:22:13 PM                 Inj :   1
                                               Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```

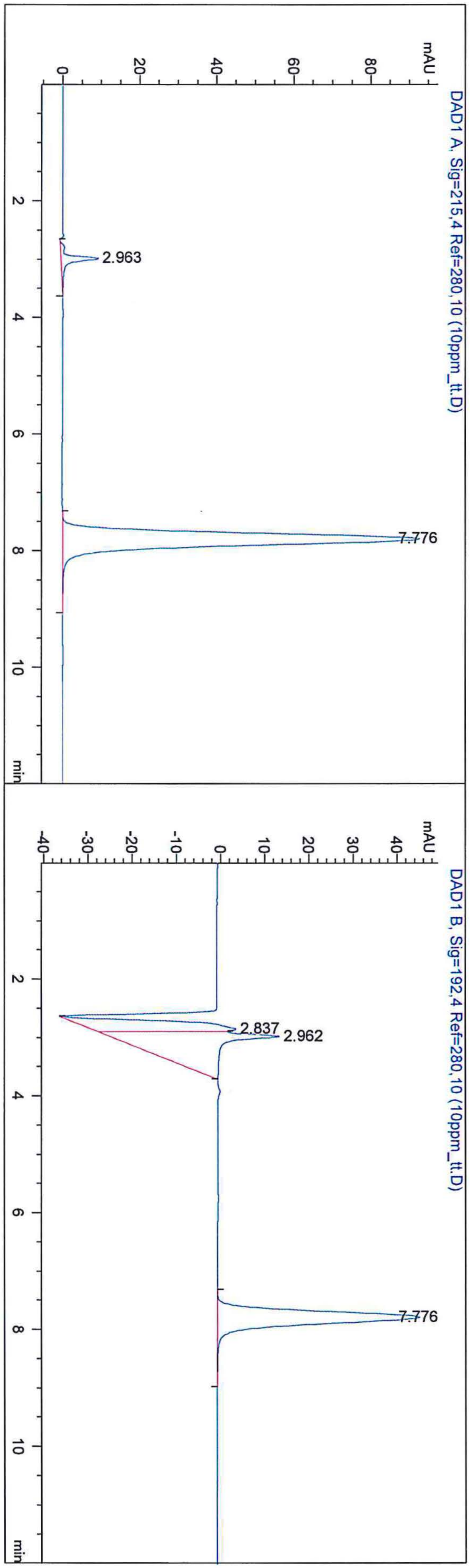

DAD1 A, Sig=215,4 Ref=280,10 (10ppm_ts.D)
mAU
0
10
20
30
40
50
60
70
2.969
3.742
2
4
6
8
10
min


DAD1 B, Sig=192,4 Ref=280,10 (10ppm_ts.D)
mAU
-40
-20
0
20
40
60
2.843
2.968
3.742
2
4
6
8
10
min

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.969 BV    0.1141  131.84694   16.00748  10.3595
   2   3.742 VB    0.1965 1140.86365   78.97409  89.6405

Totals :                  1272.71059   94.98157



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.843 BV    0.1479  370.36856   32.76344  20.1554
   2   2.968 VB    0.1731  584.52838   43.95544  31.8100
   3   3.742 BB    0.1803  882.66370   67.63577  48.0345

Totals :                  1837.56064  144.35464


=====================================================================
                          *** End of Report ***
```

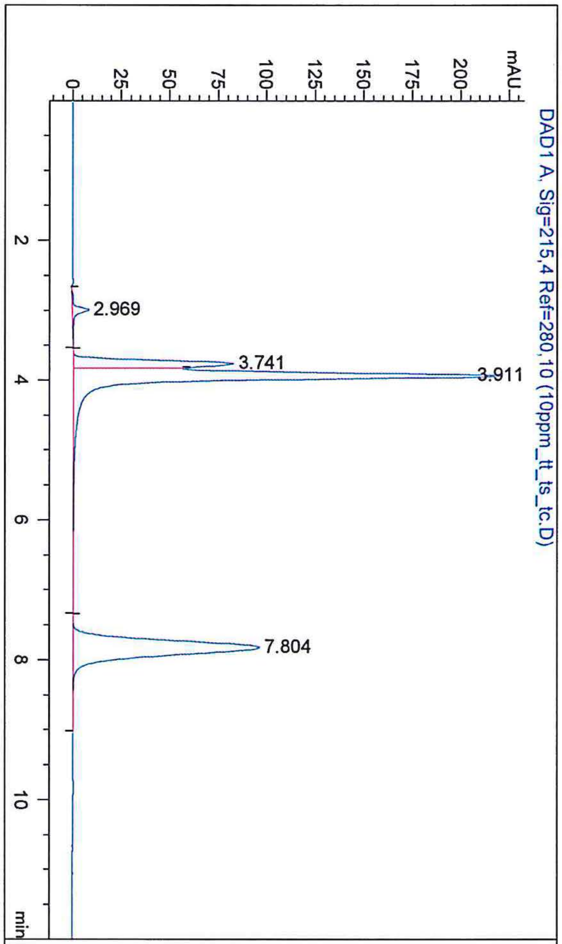
181

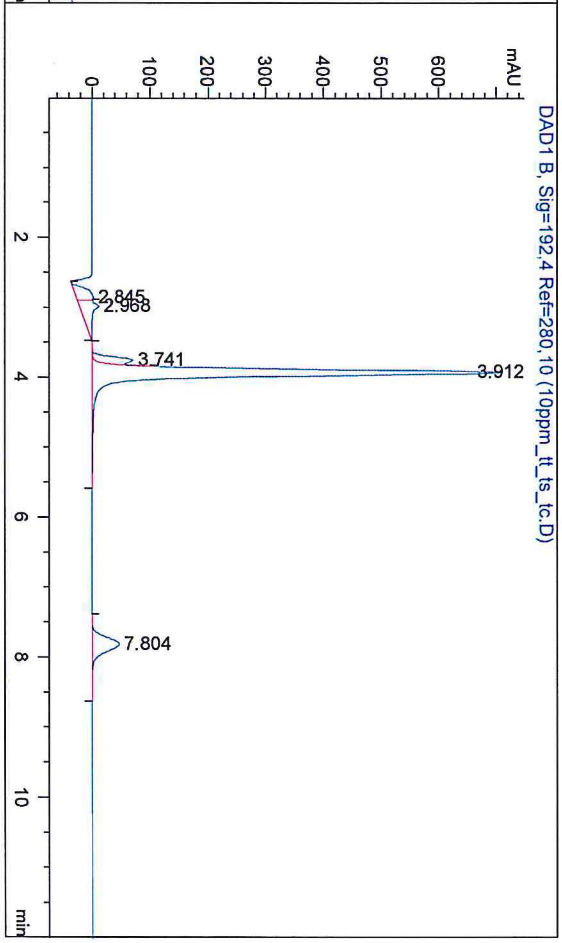
```
=====================================================================
Acq. Operator   : SYSTEM                         Seq. Line :   2
Acq. Instrument : Two Socks                       Location :   2
Injection Date  : 4/12/2017 12:38:55 PM                Inj :   1
                                                Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```


DAD1 A, Sig=215,4 Ref=280,10 (10ppm_tt.D)
mAU
0
20
40
60
80
2
4
6
8
10
min
2.963
7.776
DAD1 B, Sig=192,4 Ref=280,10 (10ppm_tt.D)
mAU
-40
-30
-20
-10
0
10
20
30
40
2
4
6
8
10
min
2.837
2.962
7.776

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.963 BB    0.1129   80.46842    9.88760   5.5243
   2   7.776 BB    0.2268 1376.16675   92.91438  94.4757

Totals :                  1456.63517  102.80198



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.837 BV    0.1526  385.13559   32.89577  21.1165
   2   2.962 VB    0.2466  757.40344   38.65010  41.5276
   3   7.776 BB    0.2271  681.31799   45.93251  37.3559

Totals :                  1823.85703  117.47838


=====================================================================
                          *** End of Report ***
```

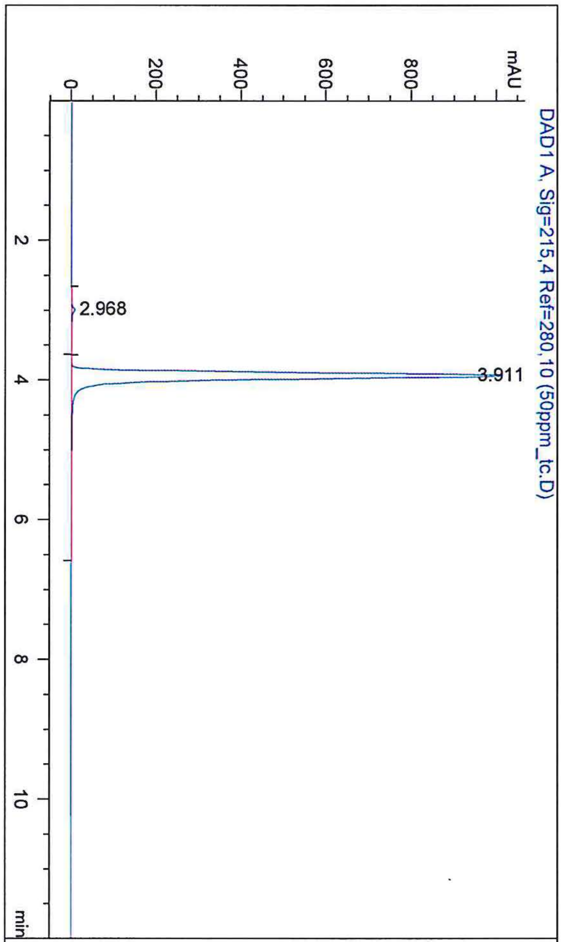
```
=====================================================================
Acq. Operator   : SYSTEM                        Seq. Line :  11
Acq. Instrument : Two Socks                      Location :   11
Injection Date  : 4/12/2017 2:48:44 PM                Inj :   1
                                               Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```

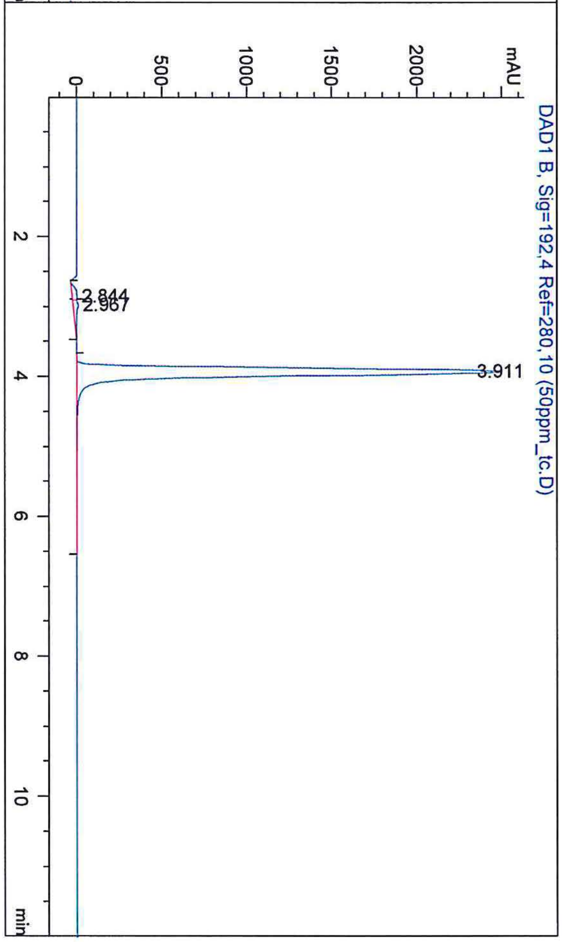

DAD1 A, Sig=215,4 Ref=280,10 (10ppm_tt_ts_tc.D)
mAU
0
25
50
75
100
125
150
175
200
min
2
4
6
8
10
2.969
3.741
3.911
7.804


DAD1 B, Sig=192,4 Ref=280,10 (10ppm_tt_ts_tc.D)
mAU
0
100
200
300
400
500
600
min
2
4
6
8
10
2.845
2.968
3.741
3.912
7.804

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.969 BB    0.1103   69.64545    8.80732   1.7700
   2   3.741 BV    0.1041  569.21094   82.87720  14.4662
   3   3.911 VB    0.1234 1888.48010  221.60965  47.9947
   4   7.804 BB    0.2244 1407.43054   96.35875  35.7691

Totals :                  3934.76704  409.65291



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.845 BV    0.1523  349.63422   29.92482   4.8256
   2   2.968 VB    0.1974  519.13831   34.14650   7.1650
   3   3.741 BV E  0.0946  418.23672   67.23679   5.7724
   4   3.912 VB R  0.1102 5261.04150  712.12000  72.6119
   5   7.804 BB    0.2242  697.37665   47.79076   9.6251

Totals :                  7245.42740  891.21886


=====================================================================
                          *** End of Report ***
```

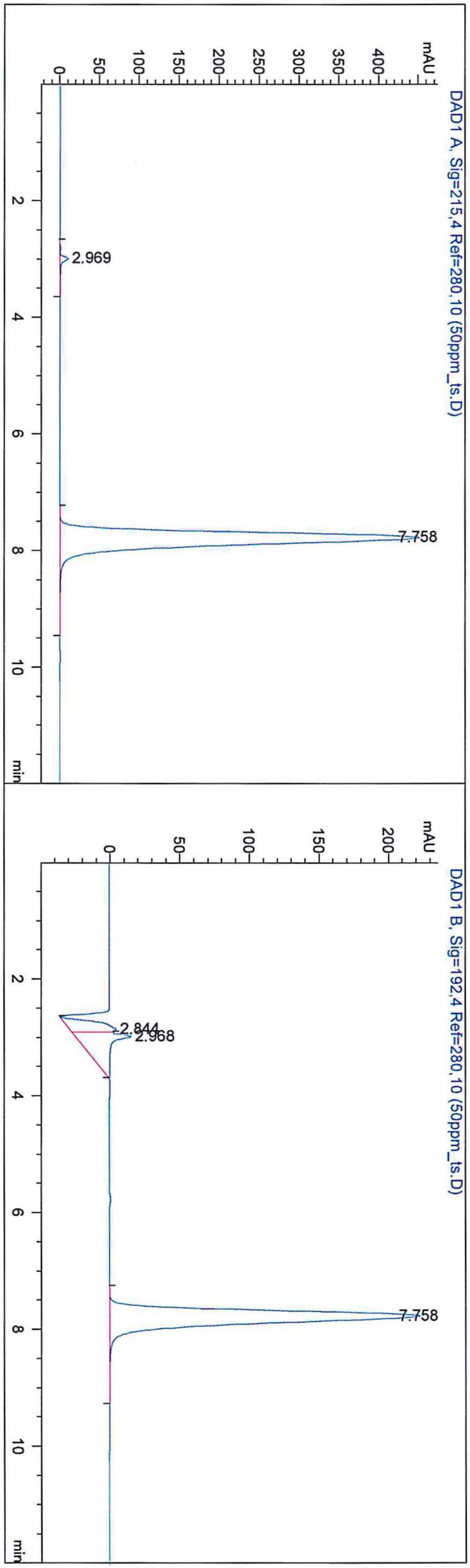
```
======================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   9
Acq. Instrument : Two Socks                        Location :   9
Injection Date  : 4/12/2017 2:19:54 PM                  Inj :   1
                                                 Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```


DAD1 A, Sig=215,4 Ref=280,10 (50ppm_tc.D)
mAU
0
200
400
600
800
2
4
6
8
10
min
2.968
3.911


DAD1 B, Sig=192,4 Ref=280,10 (50ppm_tc.D)
mAU
0
500
1000
1500
2000
2
4
6
8
10
min
2.844
2.967
3.911

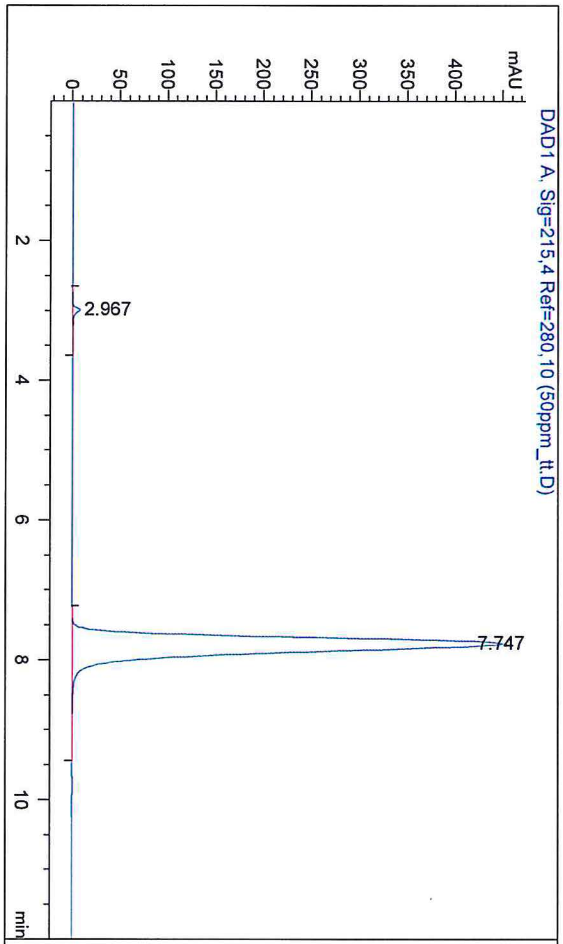
```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.968 BB    0.1161   66.99829    7.96385   0.9478
   2   3.911 BB    0.1043 7001.95166 1017.68457  99.0522

Totals :                  7068.94995 1025.64842



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.844 BV    0.1535  350.33762   29.71856   1.6537
   2   2.967 VB    0.1962  498.65961   32.63890   2.3539
   3   3.911 BB    0.1266 2.03358e4  2508.35815  95.9924

Totals :                  2.11848e4  2570.71562


=====================================================================
                          *** End of Report ***
```

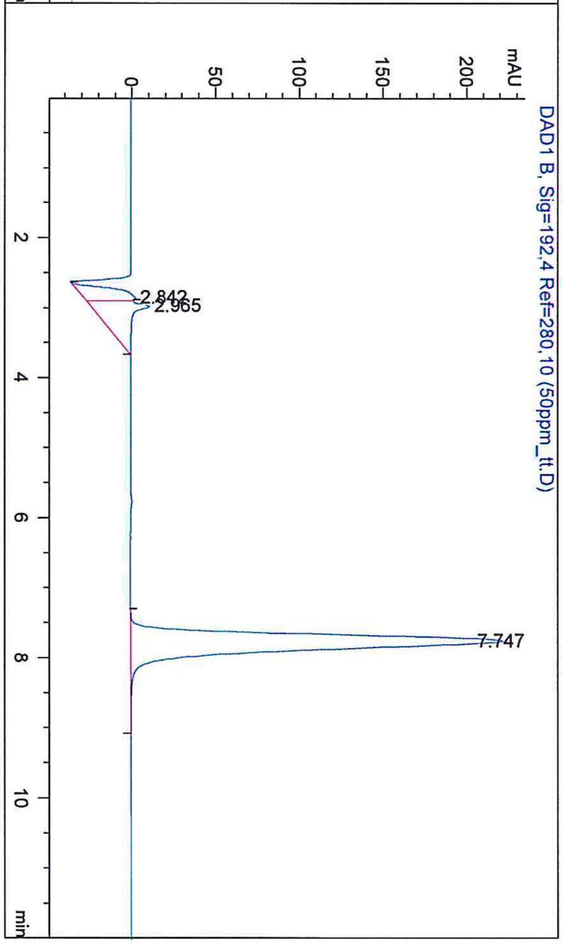
```
=====================================================================
Acq. Operator   : SYSTEM                         Seq. Line :   6
Acq. Instrument : Two Socks                       Location :   6
Injection Date  : 4/12/2017 1:36:38 PM                 Inj :   1
                                                Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```


DAD1 A, Sig=215,4 Ref=280,10 (50ppm_ts.D)
mAU
0
50
100
150
200
250
300
350
400
2.969
7.758
2
4
6
8
10
min
DAD1 B, Sig=192,4 Ref=280,10 (50ppm_ts.D)
mAU
0
50
100
150
200
2.844
2.968
7.758
2
4
6
8
10
min

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.969 BB    0.1111   87.89811   11.01880   1.2887
   2   7.758 BB    0.2279 6732.98193  451.70645  98.7113

Totals :                  6820.88004  462.72525



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.844 BV    0.1497  385.08847   33.60667   8.6189
   2   2.968 VB    0.2349  747.79492   40.21651  16.7369
   3   7.758 BB    0.2281 3335.05713  223.44603  74.6442

Totals :                  4467.94052  297.26921


=====================================================================
                          *** End of Report ***
```

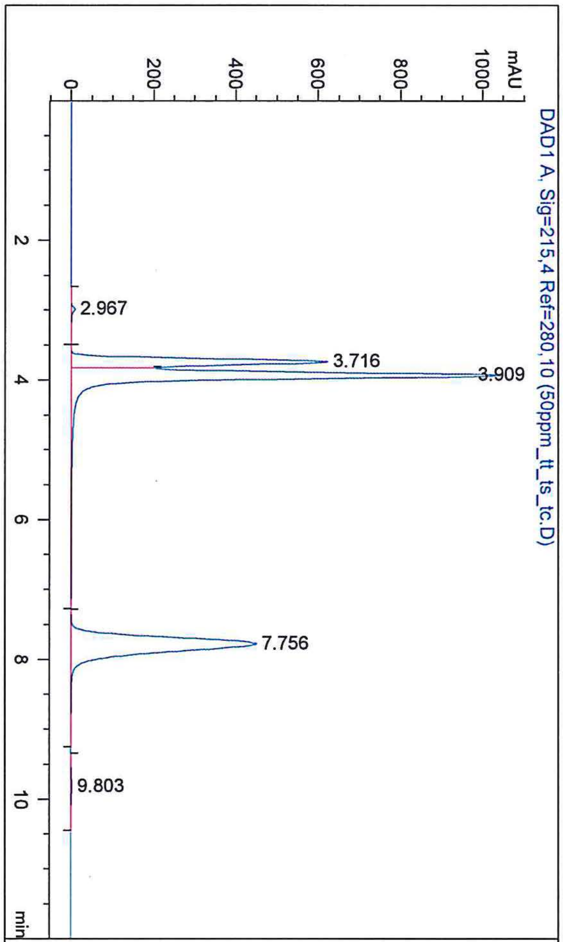
```
=====================================================================
Acq. Operator   : SYSTEM                          Seq. Line :   3
Acq. Instrument : Two Socks                        Location :   3
Injection Date  : 4/12/2017 12:53:22 PM                 Inj :   1
                                                Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```

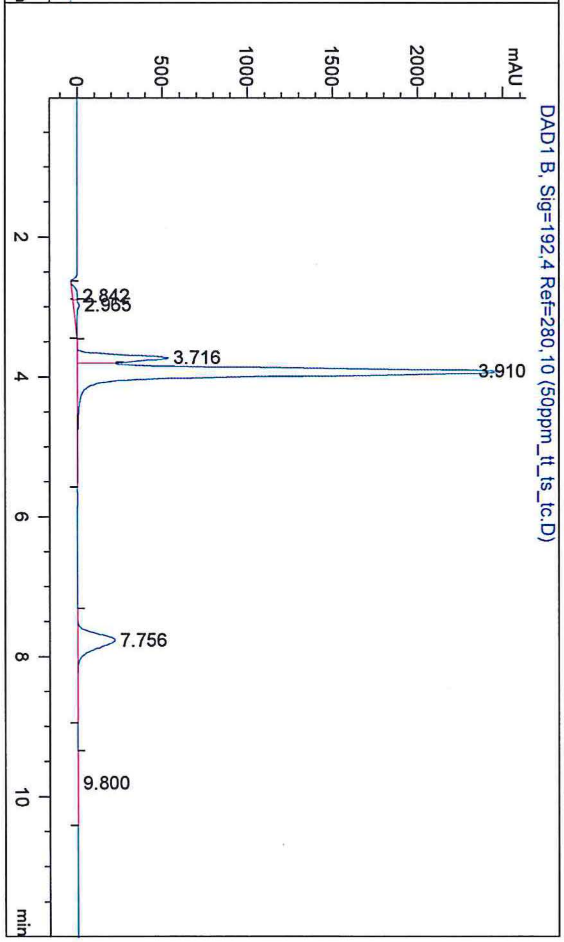

DAD1 A, Sig=215,4 Ref=280,10 (50ppm_tt.D)
mAU
0
50
100
150
200
250
300
350
400
2
4
6
8
10
min
2.967
7.747


DAD1 B, Sig=192,4 Ref=280,10 (50ppm_tt.D)
mAU
0
50
100
150
200
2
4
6
8
10
min
2.842
2.965
7.747

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.967 BB    0.1199   69.81964    7.99466   1.0265
   2   7.747 BB    0.2281 6731.83594  451.00952  98.9735

Totals :                  6801.65558  459.00418



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.842 BV    0.1552  367.92944   31.29737   8.3681
   2   2.965 VB    0.2490  700.50995   35.38481  15.9322
   3   7.747 BB    0.2283 3328.37549  222.80933  75.6997

Totals :                  4396.81488  289.49151


=====================================================================
                          *** End of Report ***
```

```
=====================================================================
Acq. Operator   : SYSTEM                         Seq. Line :  12
Acq. Instrument : Two Socks                       Location :   12
Injection Date  : 4/12/2017 3:03:10 PM                 Inj :   1
                                                Inj Volume : 25.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 50.000 µl
Sequence File   : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\Standards.S
Method          : C:\Chem32\1\Data\SULFUR\Standards 2017-04-12 12-23-04\SULFURISO60a.M (
                  Sequence Method)
Last changed    : 4/12/2017 12:23:04 PM by SYSTEM
Method Info     : SULFUR SPECIES
```


DAD1 A, Sig=215,4 Ref=280,10 (50ppm_tt_ts_tc.D)
mAU
0
200
400
600
800
1000
2
4
6
8
10
min
2.967
3.716
3.909
7.756
9.803


DAD1 B, Sig=192,4 Ref=280,10 (50ppm_tt_ts_tc.D)
mAU
0
500
1000
1500
2000
2
4
6
8
10
min
2.842
2.965
3.716
3.910
7.756
9.800

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=215,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.967 BB    0.1060   72.68671    9.63821   0.3851
   2   3.716 BV    0.1010 4120.83203  624.25714  21.8352
   3   3.909 VB    0.1136 8080.85352 1052.55298  42.8182
   4   7.756 BB    0.2236 6553.14160  450.79996  34.7233
   5   9.803 BB    0.2808   44.95182    2.41895   0.2382

Totals :                  1.88725e4  2139.66723



Signal 2: DAD1 B, Sig=192,4 Ref=280,10

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   2.842 BV    0.1496  343.28461   29.98275   1.2165
   2   2.965 VB    0.1841  496.61523   34.87189   1.7599
   3   3.716 BV    0.0979 3410.43237  538.58362  12.0861
   4   3.910 VB    0.1283 2.07030e4  2508.83618  73.3683
   5   7.756 BB    0.2236 3241.35718  222.93423  11.4869
   6   9.800 BB    0.2669   23.21482    1.23736   0.0823

Totals :                  2.82179e4  3336.44604


=====================================================================
                          *** End of Report ***
```