FERRATE IRON (Fe$^{6+}$) AS AN ALTERNATIVE METHOD FOR
THE DETOXIFICATION OF CYANIDE AND CYANIDE
SPECIES IN GOLD CYANIDATION LEACH TAILS

by
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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Masters of Science (Metallurgical and Materials Engineering).

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ABSTRACT

The oxidative properties of ferrate (VI) iron were investigated in an attempt to determine its destruction efficiency on the cyanide ion, cyanide containing species, and the resulting derivatives of the oxidative process. The species included free cyanide and the complexes of copper, nickel, silver, and thiocyanate respectively. Additionally, in an effort to harness the ferrate breakdown product of ferric hydroxide, the removal of heavy metals was also investigated. The studies were conducted in Newmont facilities on controlled synthetic solutions as well as “real world” tailings from Newmont owned properties. It was established that, irrespective of metal specie studied, cyanide detox by ferrate was achieved.
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DEDICATION

This thesis is dedicated to my amazing wife, Christy for her inexhaustible strength, support, reassurance, and belief in my abilities to always do better. And to my child to be . . . I didn’t know it until very recently, I was doing all of this for you.
CHAPTER 1

INTRODUCTION

1.1 Background

In the year 1887, three men patented a new process for the recovery of gold from its ores. John MacArthur, Robert Forester, and William Forester utilized a previously untested chemical compound made up of two simple common elements; carbon and nitrogen. Since then cyanide has remained the preferred lixiviant for the leaching of gold from most ore types.

There are generally two types of ores that are handled by a gold leaching operation; run of mine heap leach ore and millable grade ore. They again can be broken up to two additional types of ores classified by mineralogy; oxide ore, and refractory ore. In the past gold mining companies mined easily leachable oxide ore that responded well to cyanidation yielding exceptional recoveries while producing waste that was relatively innocuous. Today however, the mineralogy of existing deposits has become increasingly difficult to leach resulting in lower gold recoveries, a higher loss of gold to tails, dissolution of undesirable heavy metals, and the production of a problematic waste solution of complex cyanide and sulfur species that require sophisticated treatment techniques in order to meet the world’s strict environmental standards.

The process flow sheet in Figure 1.1 is a simplified version of Newmont’s Phoenix operation located near Battle Mountain, Nevada. Primarily a copper mine consisting of mixed copper sulfide mineralogy with low grade inclusions of gold and silver, it is a perfect example of the complexity of today’s ore bodies. As illustrated in the flow sheet, millable ore is crushed, ground, and the resulting slurry pumped into the flotation circuit where the copper sulfides are removed as a flotation concentrate. The flotation tailings, significantly lower in sulfide minerals than before, but not completely stripped of them; enter the leach circuit where a solution of lime and sodium cyanide are added. As the solution flows downhill
Figure 1.1 Phoenix Process Flow Sheet
through the eight leach tanks a counter current of activated carbon flows in the opposite direction. As it moves, solubilized gold that is complexed as dicyanoaurate adsorbs onto the carbon. The loaded carbon is stripped and the final pregnant solution reports to the electrowinning circuit.

The primary waste in the process is that of the leach tails which are pumped into the cyanide detox reactor where the weak and dissociable cyanide species (WAD) are oxidized to less than fifty parts per million, a toxicity threshold set by the International Cyanide Code for the safety of migratory birds. After leaving the reactor, the detox tails meet up with the thickener underflow and reports to the tailings impoundment where the solution is allowed to clarify and react with UV light (sunlight) over the course of several days before being recycled back into the process.

As would be expected, the leach tails entering the detox reactor contain a host of problematic species. Because the cyanide ion is not selective to the dissolution of gold and silver, heavy metals like mercury, nickel, iron, copper, and zinc react readily with cyanide to form a soluble metal-cyano species. Additionally, when highly sulfidic ore types are treated, various heavy metals, and reduced sulfur species such as thiocyanate must also be considered when planning out a waste treatment design. Table 1.1 is a partial list of major minerals associated with gold mining and would serve as an outline of what to expect concerning cyanide species or complexes that may be present in a given mining operation.

It should be noted that there are a number of other cyanide reactive minerals that occur in nature that are not included.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>% Dissolved in 24hrs</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calaverite</td>
<td>AuTe₂</td>
<td>Readily</td>
</tr>
<tr>
<td>Silver</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argentite</td>
<td>Ag₂S</td>
<td>Readily</td>
</tr>
<tr>
<td>Cerargyrite</td>
<td>AgCl</td>
<td>Readily</td>
</tr>
<tr>
<td>Proustite</td>
<td>Ag₂AsS₃</td>
<td>Sparingly</td>
</tr>
</tbody>
</table>

Table 1.1 Solubility of Selected Minerals in Cyanide solutions [5]

Reference:
- Johnston (1933)
- Leaver, Wolf, and Karchmer (1931)
### Table 1: Select Mineral and Metal Compounds

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Percent</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrargyrite</td>
<td>(\text{Ag}_3\text{SbS}_3)</td>
<td>Sparingly</td>
<td>Leaver and Woof (1931)</td>
</tr>
<tr>
<td>Copper</td>
<td>Azurite 2\text{CuCO}_3\cdot\text{Cu(OH)}_2</td>
<td>100</td>
<td>Woolf (1931)</td>
</tr>
<tr>
<td>Malachite</td>
<td>\text{CuCO}_3\cdot\text{Cu(OH)}_2</td>
<td>90.2</td>
<td>Woof (1931)</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>\text{Cu}_2\text{S}</td>
<td>90.2</td>
<td>Woof (1931)</td>
</tr>
<tr>
<td>Cuprite</td>
<td>\text{Cu}_2\text{O}</td>
<td>85.5</td>
<td>Woof (1931)</td>
</tr>
<tr>
<td>Bornite</td>
<td>\text{FeS} \cdot 2\text{Cu}_2\text{S} \cdot \text{CuS}</td>
<td>70</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Enargite</td>
<td>\text{3CuS} \cdot \text{As}_2\text{S}_5</td>
<td>65.8</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Tetrahedrite</td>
<td>\text{4Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3</td>
<td>21.9</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Chrysocolla</td>
<td>\text{CuSiO}_3</td>
<td>11.8</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>\text{CuFeS}_2</td>
<td>5.6</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Iron</td>
<td>Pyrrhotite \text{FeS}</td>
<td>Readily</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Pyrite</td>
<td>\text{FeS}_2</td>
<td>Sparingly</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Hematite</td>
<td>\text{Fe}_2\text{O}_3</td>
<td>Sparingly</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Magnetite</td>
<td>\text{Fe}_3\text{O}_4</td>
<td>Insoluble</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Siderite</td>
<td>\text{FeCO}_3</td>
<td>Insoluble</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
<tr>
<td>Lead</td>
<td>Galena \text{PbS}</td>
<td>Soluble at High Alk.</td>
<td>Lemmon (1940)</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Arsenopyrite \text{FeAsS}</td>
<td>21.1</td>
<td>Hedley and Tabachnick (1958)</td>
</tr>
</tbody>
</table>

### 1.2 Scope of Work and Objective

Current detoxification processes that have found a beneficial place in field applications include INCO (\(\text{SO}_2\)/Air), Hydrogen Peroxide, and Caro’s Acid. Although effective in specific applications, each method has its caveats. The scope of this research entailed 1) an investigation into the use of Hexavalent Iron (Super Iron) as an alternative reagent in the destruction of cyanide, cyanide species, and derivatives, 2) the determination of ferrate reaction kinetics and 3) a comparison of the economics of ferrate use to the three destruction methods afore mentioned. To this end, the experimental plan is as follows:

- **A.** Obtain high purity potassium ferrate for detox testing.
- **B.** Determine true purity of potassium ferrate salt
- **C.** Perform reaction kinetics and detoxification testing on synthetic solutions of:
  - **a)** Free Cyanide as: \(\text{CN}^-\)
b) Complex WAD cyanide as: $[\text{Ag(CN)}_2^-]$, $[\text{Cu(CN)}_3^{2-}]$, $[\text{Ni(CN)}_4]^{2-}$

c) Cyanide Leach Derived Species as: Thiocyanate ($\text{SCN}^-$)

d) Stability of Cyanide Oxidation Products: Cyanate ($\text{OCN}^-$)

D. Study the stability of the following poly-thionate species common to sulfide leaching:

a) $\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{S}_5\text{O}_6^{2-}$

E. Obtain leach tails from Newmont sites that currently employ some type detoxification circuit.

F. Perform cyanide detoxification studies on leach tails.

Being billed as a “Green Technology”, the successful study of cyanide destruction via Iron (VI) has obvious benefits to Newmont. Not only will this research add to the body of science relating to cyanide detoxification processes, it will present Newmont with an alternative choice when designing a detox circuit that is to be implemented in environmentally sensitive areas where discharge limits for cyanide, cyanide derived species, and heavy metals are of significant concern.
CHAPTER 2

LITERATURE REVIEW

2.1 Chemistry of Cyanidation

In this chapter is a brief discussion of cyanide chemistry as it pertains to the dissolution of gold, silver, copper, nickel, and sulfur bearing minerals. Although many other elements form stable complexes with cyanide, it is these five elements that cause difficulties in the context of reagent consumption and cyanide detoxification of leach tails.

2.1.1 Gold

Gold is very stable relative to the other elements on the periodic table. By exposing the metal to extreme oxidative conditions such as in the case of Aqua-Regia, a 3:1 mixture of hydrochloric and nitric acids, the stability can be effectively reduced. Although the attribute of Aqua-Regia to dissolve gold was known as far back as the 14th century, its use today for large scale gold production is not feasible. Economic constraints greatly influence every turn and bend of a process flow sheet. Choosing the correct lixiviant and understanding the downstream chemistry of that choice is of paramount importance. Over the last few decades, a variety of compounds have been tested and retested for use as an alternative to cyanide. Driven by geological/chemical challenges in such instances as a low grade heap gone acidic, or a new environmental regulation such as the newly imposed limits on cyanide leaching operations in the state of Montana, cyanide was taken off the table. A short list of alternative reagents that were tested includes ammonia, thiourea, thiosulfate, and thiocyanate. Although muted success was achieved, none had the leaching characteristics that placed cyanide into its own category with regards to extraction efficiency, kinetics, economy, and its ability to be reclaimed and recycled back into the process.

Cyanide salts, namely sodium cyanide, dissolve readily in water, dissociating into its respective ions.
NaCN\(_{(s)}\) \rightarrow \text{Na}^+ + \text{CN}^-

Figure 2.1 shows the dissociation of cyanide as a function of pH. At standard temperature and pressure (STP), the acid dissociation constant for hydrogen cyanide is pK\(_a\) = 9.31. Hence at pH 9.3, 50% of total cyanide exists as dissolved hydrogen cyanide gas, and 50% as the cyanide ion. Due to the relatively high vapor pressure of HCN\(_{(g)}\) (100 kPa at 25°C) the solution in a cyanide leach circuit is held around pH 10.2 where >90% exists as the free cyanide ion. \[3\]

This is important as the leaching of gold occurs only when a sufficient concentration of free cyanide exists in solution. Figure 2.2 describes the thermodynamic stability of the cyanide-water system as a function of pH and oxidation potential, E\(_o\). According to the following reactions, both HCN\(_{(g)}\) and free CN\(^-\) will oxidize to cyanate (OCN\(^-\)) if the oxidation potential of the system is too high.

\[
4\text{HCN}^- + 2\text{O}_2 \rightarrow 4\text{OCN}^- + 4\text{H}^+
\]

\[
3\text{CN}^- + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow 3\text{OCN}^- + 2\text{OH}^-\]

When cyanide is oxidized, it loses its ability to dissolve gold and it is therefore critical that E\(_o\) of the leach be carefully controlled as well.

The mechanism of gold dissolution by free cyanide is an oxidation reaction that forms a soluble Au(I) complex as dicyanoaurate Au(CN)\(_2^-\) as shown in the following reaction \[3\]:

\[
2\text{Au} + 4\text{CN}^- + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Au(CN)}_2^- + \text{H}_2\text{O}_2 + 2\text{OH}^-\]

It has been shown that the reduction of oxygen to the hydroxyl ion does not take place directly, but always involves the intermediate production of hydrogen peroxide \[7\]:

\[
\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{H}_2\text{O}_2 + 2\text{OH}^-\]

\[
\text{H}_2\text{O}_2 + 2\text{e}^- \leftrightarrow 2\text{OH}^-\]

Furthermore, the hydrogen peroxide formed can be used in place of oxygen for the dissolution of gold.

Since gold can be described as an electrochemical process, the reactions can be asserted to be:

1) Anodic: \(4\text{Au}^+ + 8\text{CN}^- \rightarrow 4\text{Au(CN)}_2^- + 4\text{e}^-

2) Cathodic: \(\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-\)
Figure 2.3 is a diagram of the electrochemical interaction thought to take place at the surface of a gold particle in a cyanide solution.

Figure 2.4 shows the stability regions for gold in cyanide and water. Finally, figure 2.5 shows how the regions overlap when the systems are mixed. Notice the region of gold dissolution is well within the region of OCN⁻ formation. This illustrates that, regardless of the level of control, the loss of free cyanide to oxidation is unavoidable and therefore a significant level of free cyanide must be maintained at all times and is usually done by adding sodium cyanide in excess.

![Figure 2.1 Speciation of Cyanide and Hydrogen Cyanide in Solution as a Function of pH][3]
Figure 2.2 Pourbaix Diagram of CN-H$_2$O System
Figure 2.3 Gold-Cyanide Surface Chemistry Electrochemical Illustration [7].
Figure 2.4 Pourbaix Diagram of Au-CN-H₂O System
Figure 2.5 Pourbaix Diagram Overlap Figures 3 and 4
2.1.2 Silver

Silver sits above gold electrochemical potential and frequently occurs with gold in ore bodies. Not surprisingly, metallic silver behaves similarly to gold in cyanide solutions and dissolves as follows:

\[
\text{Ag}^0 + 2\text{CN}^- \leftrightarrow \text{Ag(CN)}_2^- + e^-
\]

The Pourbaix diagram for the Ag-CN-H\(_2\)O system at 25°C and \(10^{-3}\) M [CN] is shown in Figure 2.6. Silver dissolves in the same general area as gold which allows mining operations to maintain optimum conditions for gold leaching while silver dissolves as an added bonus. Consequently, operations that leach ores containing significant amounts of silver may employ elevated cyanide concentrations to improve silver extractions and to overcome any retarding effect on gold dissolutions caused by competition for cyanide [3].

![Figure 2.6 Pourbaix Diagram of Ag-CN-H\(_2\)O System [8]](image_url)
The downstream consequences to the over-dosing of cyanide has the negative effects of leaching undesirable metals as will be described shortly, as well as adding to the elevated levels of cyanide in waste streams that must be treated in detox reactors.

2.1.3 Copper

Figure 2.7 shows the Pourbaix diagram for the Cu-CN-H₂O System at 25°C and 10⁻³ M [CN]. Copper readily dissolves in cyanide solutions to produce the dominant 3:1 ratio of copper to cyanide as [Cu(CN)₃]²⁻. Copper dissolution is undesirable with regards to consumption of cyanide and dissolved oxygen [3]. In the ore bodies where copper minerals are dominant, as is the case in the Phoenix Operation, a sulfide flotation circuit is placed before the cyanide leach circuit to remove the majority of the leachable copper. Regardless, a small percentage of copper will always reach the leach circuit where copper cyanides are formed.

![Pourbaix Diagram of Cu-CN-H₂O System](image)

Figure 2.7 Pourbaix Diagram of Cu-CN-H₂O System [8]
Nickel is a common metal found in copper and gold ore bodies. Although its minerals exist in very low concentrations, its presence must be considered when cyanide leaching is utilized. Figure 2.8 shows the Pourbaix diagram for the Ni-CN-H$_2$O System at 25°C and $10^{-3}$ M [CN]. The main complex of nickel is tetracyanonickelate, [Ni(CN)$_4$]$^{2-}$ and it forms very stable complexes at optimum gold leaching conditions.
2.1.5 Sulfur

Sulfur and its forms are extremely abundant in gold and copper ore bodies. Elemental sulfur and mineral sulfides are normally removed by pre-leach flotation circuits however a significant amount still reaches the cyanide leach circuit. Elemental sulfur and sulfide minerals react readily with cyanide to produce the thiocyanate ion, sulfide, sulfite, and polysulfide ions [3].

\[
S^0 + CN^- \rightarrow SCN^-
\]

\[
MS^{2-} + CN^- \rightarrow (M-1)S^{2-} + SCN^- + 2e^-
\]

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

Estimates state the amount of cyanide consumed by 1% sulfur exceeds 15.3 kg/ton NaCN [3]. Polythionates, also called reduced sulfur species, include thiosulfate (\(S_2O_3^{2-}\)), trithionate (\(S_3O_6^{2-}\)), tetrathionate (\(S_4O_6^{2-}\)), and pentathionate (\(S_5O_6^{2-}\)) are also common to cyanide leach systems where sulfur is present. The general form for polythionate conversation to SCN is shown below [13]:

\[
S_nO_6^{2-} + (n - 3)HCN \rightarrow (n - 3)SCN^- + S_{3-n}O_6^{2-} + (n - 3)H^+
\]

Figure 2.9 is a schematic illustration of the reaction of polythionates in aqueous solutions form thiocyanate.

2.2 Remediation of Cyanide Waste

In the mining industry today, there are several techniques widely employed for the remediation of cyanide wastes. Cyanide Detoxification can be divided into three categories: 1) Dilution, 2) Removal, and 3) Chemical Conversion. Regardless of the approach taken, the goal at the end of the day is to lower the concentration of reactive cyanides to a level acceptable by federal and international standards.

Dilution is the simplest and quickest method to reduce cyanide solution levels; however it is no longer regarded as an acceptable option. Today’s stringent discharge limits would require an extreme ratio of
Figure 2.9 Schematic Illustration of the Reaction of Polythionates in Aqueous Solutions to form thiocyanate [21]
fresh water to process water that operations in dry climates could not achieve. In such operations treated waste water is recycled back into the process where it is needed.

Another method of cyanide waste treatment is passive removal. The absorption of cyanide by soils, ores, and in some instances organic animal waste has been shown to be effective. However, the sheer volume of a mining waste stream and the slow conversion of a passive system are not conducive. The only other option is chemical conversion.

2.2.1 Caro’s Acid

Caro’s acid is the common name for peroxymonosulfuric acid, H₂SO₅. It is produced by the flash reaction of 70% hydrogen peroxide and concentrated sulfuric acid. Extreme heat is generated from the reaction so it must be mixed in a chilled reactor as is shown in Figure 2.1 [25]:

\[
H_2O_2 + H_2SO_4 \rightarrow H_2SO_5 + H_2O + \Delta H
\]

Figure 2.10 Caro’s Acid Reactor Plant [4]
Due to its instability, Caro’s acid is injected into a detox reactor as quickly as it is generated. The conversion of cyanide to cyanate is rapid at a pH between 7 and 10. Within minutes the cyanide species are well below the 50 mg/L limit required for discharge to tailings [6]:

$$\text{CN}^- + \text{H}_2\text{SO}_3 \rightarrow \text{OCN}^- + \text{SO}_4^{2-} + 2\text{H}^+$$

The theoretical usage of Caro’s acid in the process is 4.39g H$_2$SO$_3$/g CN oxidized, but in practice 5.0g to 15g H$_2$SO$_3$/g CN is required [4].

As cyanide is oxidized the Caro’s acid is reduced to sulfuric acid which is immediately neutralized in the lime fortified environment of the reactor. The oxidation of weakly bound complexes such as those of copper (I) and nickel (I) occurs in a similar manner, according to the following reaction [13]:

$$\text{M(CN)}_4^{2-} + 2\text{SO}_3^- + 10\text{OH}^- \rightarrow \text{M(OH)}_2 + 4\text{OCN}^- + 8\text{H}_2\text{O} + 4\text{SO}_4^{2-}$$

The desirable oxidation strength, Eh 1.84V [13] and reactivity of Caro’s acid is also its caveat. Caro’s acid is not selective to the oxidation of cyanide; it is reactive to most constituents of a reactor pulp. Due to that fact, Caro’s acid is dosed in high excess which produces unwanted side reactions. One unwanted reaction is the hydrolysis of cyanate to ammonia [19]:

$$\text{OCN}^- + 2\text{H}_2\text{O} \rightarrow \text{CO}_2(g) + \text{NH}_3(g) + \text{OH}^-$$

Another is thiocyanate, present in the leaching of sulfide ores, and is a huge consumer of Caro’s Acid at a 4:1 ratio according to reaction 1-10:

$$\text{SCN}^- + 4\text{SO}_3^- + 10\text{OH}^- \rightarrow 5\text{SO}_4^{2-} + \text{OCN}^- + 9\text{H}_2\text{O}$$

Caro’s Acid is also consumed by mineral species such as those shown in table 1.1. At Newmont’s Phoenix Operation in Nevada, Pyrrhotite (FeS) is a very common non-value mineral that is suppressed during sulfide flotation. As it travels through the leach and into the Caro’s Acid reactor, the mineral is oxidized to form ferric hydroxide and sulfate. Such complex pulp characteristics are said to “quench” the Caro’s Acid and often times the only remedy is to increase the dosage rate. The following table shows the estimated cost of a Caro’s Acid reactor as of 2012 assuming a 50 mg/L CN$_{x/wad}$ feed at 1050 m$^3$/hr.
Table 2.1  Estimated Operating Costs of Caro’s Acid Detox Plant Courtesy of Newmont Water Treatment Group

<table>
<thead>
<tr>
<th></th>
<th>Amount (kg/day)</th>
<th>Cost ($/kg)</th>
<th>Total Cost ($/day)</th>
<th>Total Cost ($/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide</td>
<td>4,176</td>
<td>0.84</td>
<td>3,508</td>
<td>1,281,000</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>18,984</td>
<td>0.11</td>
<td>2,088</td>
<td>763,000</td>
</tr>
<tr>
<td>Lime Slurry</td>
<td>1,000</td>
<td>0.13</td>
<td>129</td>
<td>48,000</td>
</tr>
<tr>
<td>Power</td>
<td></td>
<td></td>
<td>72,000</td>
<td></td>
</tr>
<tr>
<td>Labor</td>
<td></td>
<td></td>
<td>100,000</td>
<td></td>
</tr>
<tr>
<td><strong>Total Operating Cost</strong></td>
<td></td>
<td></td>
<td><strong>2,262,000</strong></td>
<td></td>
</tr>
</tbody>
</table>

2.2.2 $\text{SO}_2$/AIR

A widely used alternative to Caro’s Acid is $\text{SO}_2$/Air. Sulfur dioxide Assisted Oxidation as it is known in the mining industry was first patented in 1980 by the International Nickel Company and thus coined the INCO Process of cyanide destruction. See figure 2.11.

The process uses a mixture of sulfur dioxide and oxygen (provided by sparging with air) in the presence of $\text{Cu}^{2+}$ to oxidize free cyanide to cyanate [14]:

\[
\text{CN}^- + \text{SO}_2 + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{OCN}^- + \text{SO}_4^2- + 2\text{H}^+
\]

Thiocyanate, although significantly slower, will is oxidized by $\text{SO}_2$ according to the following reaction [28]:

\[
\text{SCN}^- + 4\text{SO}_2 + 4\text{O}_2 + 5\text{H}_2\text{O} \rightarrow \text{OCN}^- + 5\text{SO}_4^2- + 10\text{H}^+
\]

The theoretical usage of $\text{SO}_2$ in the process is 2.46g $\text{SO}_2$/g CN$^-$ oxidized, but in practice the actual usage ranges from about 3.5g – 5.0g $\text{SO}_2$/g CN$^-$ oxidized [4]. The $\text{SO}_2$ in the reaction can be supplied either as a
liquid sulfur dioxide or a sulfur salt such as sodium metabisulfite. The copper catalyst is added as copper (II) sulfate to a concentration of 10 – 50mg/L, depending on the availability of native copper in a reactor.

**Figure 2.11** Reactor Schematic for SO₂/Air Cyanide Detoxification [4]

Similarly as with Caro’s Acid, cyanide species are decomposed to free cyanide and metal ions. As the liberated cyanide is further oxidized to cyanate, the free metals fall out as hydroxides in the high pH environment of the reactor. The removal of ferric cyanide is affected through precipitation with previously liberated metals.

\[ 2M^{2+} + \text{Fe(CN)}_{6}^{4-} \rightarrow \text{M}_2\text{Fe(CN)}_6 \]

Relative to Caro’s Acid destruction, INCO is especially selective to cyanide compounds. If there is a notable drawback it would be its slower reaction kinetics. While Caro’s drops cyanide levels below acceptable limits within minutes, the resident time for INCO is thirty minutes to one hour to reach
sufficient discharge levels. The following table shows the estimated cost of a Caro’s Acid reactor as of 2012 assuming a 50 mg/L CN$_{wad}$ feed at 1050 m$^3$/hr.

Table 2.2  Estimated Operating Costs of SO$_2$/Air Cyanide Detox Plant Courtesy of Newmont Water group

<table>
<thead>
<tr>
<th></th>
<th>Amount (kg/day)</th>
<th>Cost ($/kg)</th>
<th>Total Cost ($/day)</th>
<th>Total Cost ($/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metabisulfite Solution</td>
<td>12,000</td>
<td>0.40</td>
<td>4,800</td>
<td>1,752,000</td>
</tr>
<tr>
<td>Copper Sulphate Solution</td>
<td>429</td>
<td>2.00</td>
<td>858</td>
<td>314,000</td>
</tr>
<tr>
<td>Lime Slurry</td>
<td>4680</td>
<td>0.13</td>
<td>604</td>
<td>221,000</td>
</tr>
<tr>
<td>Power (blowers)</td>
<td></td>
<td></td>
<td></td>
<td>500,000</td>
</tr>
<tr>
<td>Power (agitator)</td>
<td></td>
<td></td>
<td></td>
<td>148,000</td>
</tr>
<tr>
<td>Labor</td>
<td></td>
<td></td>
<td></td>
<td>100,000</td>
</tr>
<tr>
<td>Total Operating Cost</td>
<td></td>
<td></td>
<td></td>
<td>3,033,000</td>
</tr>
</tbody>
</table>

2.3 Ferrate Production

Iron sits at number 26 on the periodic table and is the fourth most abundant element on earth. Iron exists as elemental iron Fe$^0$, along with plenty of minerals in the ferrous Fe(II) and Ferric(III) oxidation state. In addition to the three stable oxidation states, areas of intense oxidation have caused the occurrence of the higher oxidation states of (IV), (V), (VI), and (VIII). These higher states of iron are known as ferrates and it has been shown that Fe (VI) is the most stable and therefore easiest to study. Ferrate(VI) which was first observed by Stahl in 1902 when he conducted an experiment detonating a mixture of saltpeter (potassium nitrate) and iron filings, and dissolved the molten residue in water. This colored solution was subsequently identified as potassium ferrate. Eckenber and Becquerel in 1834 detected the
same color when they heated red mixtures of potash (potassium hydroxide) and iron ores. Similarly, in 1840, Fremy hypothesized this color to be an iron species with high valence, but its formula was incorrectly suggested to be FeO₃ [10]. But, because of its stability and cumbersome of its synthesis, it was not used nor studied further.

A variety of methods for the production of a stable ferrate salt can be broken down into dry oxidation, wet oxidation, and electrochemical synthesis. Dry synthesis is simply a high temperature fusion of a molar mixture of iron oxide (Fe₂O₃) and sodium peroxide (Na₂O₂) under atmospheric conditions to yield a 100% sodium ferrate salt in to form of Na₄FeO₅. On the other hand, wet oxidation is a combination of aqueous ferric iron and a strong liquid oxidizer such as Caro’s Acid [7] or sodium hypochlorite in a heavy caustic solution. The reaction produces the ferrate FeO₄²⁻ ion at a concentration between 10 – 15%. Stable for only a few hours, many tedious separation steps are required, including final recrystallization to obtain a 90% pure product [18].

The patent [6] for the production of a pure potassium ferrate salt is held by Lynntech, Inc. located in College Station, Texas. The basic principle is as follows: In an electrochemical cell two cast iron rods (cathode and anode) are submerged in a solution of 50% potassium hydroxide, connected to a power supply of about 6amps. As the anode steel oxidizes pure potassium ferrate salt in the form of K₂FeO₄ falls to the bottom of the cell. Since potassium ferrate is paramagnetic, it can be collected and concentrated by magnetic separation. Hydrogen gas is produced at the cathode. Figure 2.12 is a diagram of the electrochemical cell for producing potassium ferrate.

**Anode Reaction:**

\[ \text{Fe}^0 + 8\OH^- \rightarrow \text{FeO}_4^{2-} + 4\H_2\O + 6\text{e}^- \]

**Cathode Reaction:**

\[ 2\H_2\O + 2\text{e}^- \rightarrow \H_2 + 2\OH^- \]

**Overall Reactions:**

\[ \text{Fe}^0 + 2\OH^- + 2\H_2\O \rightarrow \text{FeO}_4^{2-} + 3\H_2(\text{g}) \]

\[ \text{FeO}_4^{2-} + 2\K^+ \rightarrow \K_2\text{FeO}_4(\text{s}) \]
Figure 2.12 Electrochemical Cell for Ferrate Synthesis [1]

2.4 Ferrate Chemistry

Potassium Ferrate in solution has a characteristic deep violet color. When dissolved in deionized water, effervescence occurs as oxygen is evolved followed by an intense jump in pH as the hydroxide ion forms. The stability of the ferrate ion depends strongly on the ferrate concentration dosed and the pH of the solution. At a high pH a 0.025M ferrate solution is stable for about one hour as the FeO₄²⁻ ion. But, interestingly, at a slight rise in concentration to 0.030M, almost all ferrate ions are decomposed to ferric hydroxide in the same amount of time [1]. The stability in 10M potassium hydroxide is on the order of weeks in a pure solution as long as Ni²⁺ and Co²⁺ are not present [32]. However, nitrate salts of Cu²⁺, Fe³⁺, Zn²⁺, Pb²⁺, Ba²⁺, Sr²⁺, Cr²⁺, Mg²⁺ and other salts including K₂Zn(OH)₄, KIO₄, K₂B₂O₅, K₂PO₄, Na₂P₂O₇, Na₂SiF₆, Na₂SiO₃, Na₂MoO₄ and Na₂WO₄ have no effect on the stability of K₂FeO₄ [32]. A 0.5 M K₂FeO₄,
solution, containing KCl, KNO₃, NaCl and FeOOH was studied to observe the ferrate(VI) stability in the presence of these salts. It was found that the ferrate (VI) decomposed rapidly in the initial stage and appeared relatively stable at low ferrate concentrations when KCl and KNO₃ were present [33]. Phosphate was shown to retard the ferrate (VI) decomposition.

The overall stability of ferrate in aqueous solution increases with increasing pH. At a pH > 9.0 ferrate was stable for hours at a time, but as the pH was lowered, ferrate degradation increased to the point of spontaneous decomposition in acidic conditions. Figure 2.13 shows the stability of a 0.001M ferrate solution.

Temperature dependence data showed that Ferrate solutions are relatively stable at low temperature conditions (0.5°C). In comparison, a 0.01M solution of ferrate was reduced by 10% at a constant temperature of 25°C and almost unchanged at 0.5°C for a period of two hours [35].

![Figure 2.13 Change in Ferrate Concentration as a function of pH](image-url)
Ferrate undergoes molecular changes over the entire pH range as well as a change in oxidation potential as a function of pH. Studies have reported that three unstable protonated forms of ferrate exist, along with the stable FeO$_4^{2-}$ ion. See figure 2.14.

![Figure 2.14 Speciation of Ferrate (VI) in Solution as a function of pH [34]](image)

The ferrate iron (Fe$^{6+}$) has proven to be a very powerful oxidant at very low doses as well as an effective coagulant and disinfectant for wastewater treatment processes. [1, 10] The oxidizing power increases from chromium to manganese to iron. Table 2.3 is a list of common oxidants used in the wastewater industry. At first glance it is apparent that ferrate has an oxidation potential greater than that of ozone, an extremely effective, but expensive method for the disinfection of treated wastewater. Even the most widely used chlorine based chemicals do not match up. The major interest in ferrate as an alternative has to do with its rather innocuous breakdown product of iron (III) hydroxide, an effective coagulant for co-precipitation of heavy metals.
Table 2.3 Redox Potential for the common oxidants used in water and wastewater treatment [34]

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Reaction</th>
<th>$E^0, V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>$\text{Cl}_2(g) + 2e^- \leftrightarrow 2\text{Cl}^-$  [ClO^- + \text{H}_2\text{O} + 2e^- \leftrightarrow \text{Cl}^- + 2\text{OH}^-]</td>
<td>1.358</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>$\text{HClO} + \text{H}^+ + 2e^- \leftrightarrow \text{Cl}^- + \text{H}_2\text{O}$</td>
<td>1.482</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>$\text{ClO}_2^{\text{aq}} + e^- \leftrightarrow \text{ClO}_2^-$</td>
<td>0.954</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>$\text{ClO}_4^- + 8\text{H}^+ + 8e^- \leftrightarrow \text{Cl}^- + 4\text{H}_2\text{O}$</td>
<td>1.389</td>
</tr>
<tr>
<td>Ozone</td>
<td>$\text{O}_3 + 2\text{H}^+ + 2e^- \leftrightarrow \text{O}_2 + 2\text{H}_2\text{O}$</td>
<td>2.076</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \leftrightarrow 2\text{H}_2\text{O}$</td>
<td>1.776</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \leftrightarrow 2\text{H}_2\text{O}$</td>
<td>1.229</td>
</tr>
<tr>
<td>Permanganate</td>
<td>$\text{MnO}_4^- + 4\text{H}^+ + 3e^- \leftrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$</td>
<td>1.679</td>
</tr>
<tr>
<td></td>
<td>$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$</td>
<td>1.507</td>
</tr>
<tr>
<td>Chromate</td>
<td>$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \leftrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$</td>
<td>1.33</td>
</tr>
<tr>
<td>Ferrate(VI)</td>
<td>$\text{FeO}_4^{2-} + 8\text{H}^+ + 3e^- \leftrightarrow \text{Fe}^{3+} + 4\text{H}_2\text{O}$</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>$\text{FeO}_4^{2-} + 8\text{H}_2\text{O} + 3e^- \leftrightarrow \text{Fe(OH)}_3 + 8\text{H}_2\text{O}$</td>
<td>0.70</td>
</tr>
</tbody>
</table>

The use of ferrate iron for the oxidation of organic and inorganic constituents present in natural waters is of great importance to environmental remediation strategies. Heavy metals, free or complexed, hydrogen sulfide, ammonia, and organic pollutants that pass through conventional wastewater treatment unaltered show excellent reactivity with ferrate iron. The mechanism is thought to be a one and two electron process and its kinetics ferrate reduction may be demonstrated as:

$$-\frac{d[\text{Fe(VI)}]}{dt} = k_P [\text{Fe(VI)}][P]$$

27
Where $k_p$ is the second-order rate constant for the reaction and $[P]$ is the concentration of the oxidized species [29].
CHAPTER 3

EXPERIMENTAL METHODS

This section is broken into three categories: Materials, Experimental Procedures, and the Analytical Chemistry of Cyanide. It should be noted that all costs associated with the following experimentation with regards to reagents, analytical testing, and labor, was provided by Newmont Metallurgical Services located in Englewood, Colorado in 2011 and 2012.

3.1 Materials

Electrochemically produced potassium ferrate salt (>90%) was acquired from Lynntech Inc. through Sigma Aldrich. The actual purity was later determined and will be discussed in section 3.4 of this thesis.

The following chemicals were obtained from Sigma Aldrich in the highest purity form available: Copper(I) cyanide, Nickel(II) cyanide, Silver(I) cyanide, Sodium Cyanide, and Potassium Thiocyanate. From the previous chemicals, solutions of 10 mg/L (as CN⁻) concentrations of Tricyanocuprate [Cu(CN)₃]²⁻, Tetracyanonickelate [Ni(CN)₄]²⁻, dicyanoargentate [Ag(CN)₂]⁻, a solution of 1000 mg/L free cyanide [CN⁻], and 1000 mg/L thiocyanate as [SCN⁻] were prepared according to approved methods.

Five liters of unadulterated Leach Tails at 40% solids were obtained from Newmont’s Phoenix Operation.

All other chemicals used in the analysis of the detox products, calibration of instrumentation, and certified reference materials were of the highest quality available obtained from ISO 17025 accredited laboratories.

Glassware used in all experiments was acid washed and rinsed with deionized water as to be certain analytical products of interest were not sourced to contamination.
High precision analytical balances capable of weighing to 0.0001g were used in the experiments and were calibrated according to ISO 17025 accredited calibration laboratories.

3.2 Experimental Procedures

All synthetic cyanide solutions, regardless of metal complex, were prepared at 10mg/L (0.38mM) as the CN⁻ ion in 0.01M sodium hydroxide. Thiocyanate was prepared as 10mg/L (0.17mM) SCN⁻. Solutions were prepared in an acid washed 100ml class A volumetric flask and mixed thoroughly.

The 10mg/L solutions were transferred to an acid washed 250 ml Erlenmeyer reaction flask containing an acid washed teflon stir-bar, placed upon a stir-plate, and stirred at a rate of 60 RPM.

Before individual reactions were started, the initial cyanide concentration was measured and labeled as $T=0$ in a logbook. After the initial measurement solid potassium ferrate was carefully weighed to a precision of 0.0001g on a ISO 17025 calibrated analytical balance. The potassium ferrate was carefully added to the stirring solution and the measurement of the cyanide oxidation began.

A measurement of the cyanide level was taken every 85 seconds, an interval of time equivalent to the instrument’s injection to peak start. Measurements were taken until the cyanide concentration fell below the instruments detection limit for cyanide. If the cyanide did not fall below the detection limit, but rather leveled out, the measurements were stopped; a fresh 10mg/L cyanide solution prepared, and reacted with a doubling of the potassium ferrate dose. The procedure was repeated until the cyanide level below detection or showed no response to further oxidation.
3.3 Analytical Procedure for Cyanide in Solution

The technological complexity of analytical instrumentation used in the analysis of cyanide containing wastes is directly related to the complexity of the cyanide chemistry itself. Whatever the procedure, it must be applicable to the characteristics of the sample being tested. Its dynamic linear range, sensitivity to matrix changes (robustness), and the desired level of detection must be considered.

The chosen method for the testing of the experiments in this study is known in the field of analytical chemistry is Flow Injection Gas Diffusion Amperometry. Its simplistic design is what makes it such a valuable tool for the measurement of free and weakly bound metal cyanides. The method consists of three steps: 1) Sample pretreatment, 2) Gas Diffusion, and 3) Amperometric detection. The manifold for this method of analysis is shown in figure 3.1. Starting at the left of the schematic are three liquid streams. The top stream is a continuous flow of acceptor solution (0.25N NaOH). The middle stream is a continuous flow of donor solution (1N HCl). The bottom stream is the sample stream that is injected in timed increments controlled by a switching valve that is not shown here. As the cyanide containing sample (as free cyanide and/or complex cyanide) meets up with the HCl, they are mixed in a mixing coil where the cyanide is converted to hydrogen cyanide gas. Next the stream enters the bottom half of the gas diffusion cell while the sodium hydroxide acceptor solution flows through the top half. Hydrogen cyanide travels across a selectively permeable membrane that separates the two streams and is absorbed into the hydroxide as the free CN\textsuperscript{-} ion which then flows into a Ag/AgCl amperometric cell where the voltage change is measured and is proportional to cyanide concentration according to the following reaction:

\[ \text{CN}^- + \text{Ag}^0 \rightarrow [\text{Ag(CN)}_2]^+ + e^- . \]

See Appendix D of this Thesis for the EPA Promulgated Method OIA-1677.
Figure 3.1 Schematic of Flow Injection Gas Diffusion Amperometry [22]
3.4 Determination of the Potassium Ferrate Salt Purity

The electrolytically produced potassium ferrate that was produced by Lynntech, Inc. and purchased through Sigma Aldrich has a stated purity of > 90%. In order to determine the accurate ferrate dosage in the detox studies, true assay purity was needed.

Assuming the purity to be 100%, a 100 mg/L solution of potassium ferrate as the ferrate ion (FeO$_4^{2-}$) was prepared by dissolving 0.01652g in 2% mixture of hydrochloric and nitric acid to a fixed volume of 100ml. The solution was submitted to the analytical laboratory for metals assay. Calculations and results are shown below.

Table 3.1 Calculation of potassium ferrate needed to prepare 100mg/L solution of ferrate ion.

<table>
<thead>
<tr>
<th></th>
<th>g/mol</th>
<th>% by Weight</th>
<th>100mg/L Ferrate Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$FeO$_4$</td>
<td>198.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K (2)</td>
<td>78.2</td>
<td>39.5</td>
<td></td>
</tr>
<tr>
<td>FeO$_4$</td>
<td>119.8</td>
<td>60.5</td>
<td>100 / 0.605 = 165.3 mg K$_2$FeO$_4$</td>
</tr>
</tbody>
</table>

Table 3.2 ICP-OES Expected Results and Actual Results

<table>
<thead>
<tr>
<th></th>
<th>mg/L</th>
<th></th>
<th>mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>65.3</td>
<td>Actual</td>
<td>71.0</td>
</tr>
<tr>
<td>Fe</td>
<td>46.5</td>
<td></td>
<td>46.7</td>
</tr>
</tbody>
</table>

Based on the exceptional return on the iron concentration and the higher than expected potassium value, a potassium impurity is expected. By multiplying the K impurity by the dilution factor (100/0.01653g) produced from solution preparation, the percentage of potassium contamination is calculated.

$$71.0 \text{ mg/L} - 65.3 \text{ mg/L} = (5.7 \text{ mg/L K})(6050) = 34,480 \text{ mg/L} = 3.48\% \text{ K Impurity}$$
Literature suggests that potassium ferrate is isomorphic with potassium sulfate which may account for the possible bias. A second solution of the same concentration was prepared and submitted for Sulfate analysis by ion chromatography. Since the potassium impurity was analyzed to be 3.48\%, a sulfate value of 14 mg/L is expected.

\[
(96 \text{ g/mol SO}_4)(5.7 \text{ mg/L K}) / (39 \text{ g/mol K}) = 14 \text{ mg/L SO}_4
\]

The actual sulfate result by Ion Chromatography was about 12 mg/L; a result that confirms the isomorphic effect. Therefore the potassium ferrate salt used in the cyanide detox experiments of this study is calculated to be 97\% pure.
CHAPTER 4

FERRATE OXIDATION TESTING AND RESULTS

4.1 Free Cyanide [CN⁻]

A 100 ml solution of 10 mg/L (0.0038M) free cyanide as the CN⁻ ion was prepared in a 0.01M NaOH matrix and transferred to a stirred 250 ml Erlenmeyer reaction flask. The initial concentration of cyanide, T=0, measured at 10.4 mg/L (0.4mM). To the stirring solution a 0.0122g dose of solid potassium ferrate was added. The salt dissolved instantly and produced a deep violet color that persisted throughout the experiment. Eighty-five seconds after ferrate addition, the first reading was measured. All readings that followed occurred in eighty-five second intervals.

The mixing of the sample and the analysis was allowed to continue undisturbed until no change in cyanide concentration was detected which, in the case of a 0.0122g dosage, corresponded to a total reaction time of about 40 minutes. See Figure 4.1. The pH remained constant throughout the reaction.

![Figure 4.1 Cyanide Oxidation with 0.0122g Potassium Ferrate](image)

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CN}]_0$</td>
<td>10.4 mg/L</td>
</tr>
<tr>
<td>$[\text{CN}]_f$</td>
<td>0.20 mg/L</td>
</tr>
<tr>
<td>$K_2\text{FeO}_4$ (g)</td>
<td>0.0122g</td>
</tr>
<tr>
<td>pH</td>
<td>11</td>
</tr>
<tr>
<td>$T_0-T_f$</td>
<td>38 min</td>
</tr>
</tbody>
</table>
As can be seen in figure 4.1, the cyanide concentration did not drop below the 2ug/L (7.7 X 10^{-7} M) detection limit of the instrument. The experiment with free cyanide was repeated with a fresh cyanide solution and a doubling of the ferrate addition.

A fresh solution of free cyanide was prepared and its initial concentration, T=0, measured at 10.3mg/L (0.4mM). To the stirring solution 0.0199g potassium ferrate was added and the cyanide concentrated measured in eighty-five second intervals.

The mixing of the sample and the analysis was allowed to continue undisturbed until the cyanide concentration fell below instrument detection, which corresponded to a total reaction time of about 15 minutes. See Figure 4.2.

*Since a 20mg dose of potassium ferrate successfully oxidized 100% of the measurable cyanide, the 20mg dose was chosen as the minimum starting weight for all experiments that followed.*

![Graph showing cyanide oxidation with 0.0199g Potassium Ferrate](image)

**Figure 4.2 Cyanide Oxidation with 0.0199g Potassium Ferrate**
It is believed that the oxidation of free cyanide by the ferrate ion is dictated by the following reaction at a near 1:1 stoichiometric ratio in alkaline conditions:

\[
2\text{FeO}_4^{2-} + 3\text{CN}^- + \text{OH}^- \rightarrow 2\text{Fe(OH)}_3 + 3\text{OCN}^- 
\]

It is also believed that the kinetics of the cyanide oxidation by ferrate follow the first-order rate law shown as \( \ln [A] = -kt + \ln [A]_0 \) which can also be written as \( A = A_0 e^{-kt} \).

It has been shown that the reaction rate is dependent upon the concentration of ferrate. The first order reaction can be shown as:

\[
\frac{d[A]}{d[t]} = k[\text{Fe(VI)}]^n[A] 
\]

The results were tested graphically for zero, first, and second-order kinetics and it was found that only the first-order rate law produced a straight line. See figure 4.3 and 4.4.

---

**Figure 4.3** Rate Constant of Cyanide Oxidation 0.0122g Potassium Ferrate

![Graph showing the reaction rate constant](image-url)
In order to determine the formation of oxidation products, a third 10mg/L cyanide solution was prepared and its initial concentrated was measured to be 10.3 mg/L CN\(^-\). To the stirring solution a 0.0200g dose of potassium ferrate was added and the mixture allowed to react for fifteen minutes. Every eighty-five seconds a 5ml aliquot was taken from the reaction flask and quenched in a solution 0.1N sodium arsenite consume the excess ferrate and stop the oxidation process. Over the course of 15 minutes, ten samples were drawn and quenched. The corresponding solutions were submitted for cyanide (OCN\(^-\)) analysis ion by Ion Chromatography. The results are shown in figure 4.5.
4.2 Thiocyanate as $[\text{SCN}^-]$  

In this experiment a 100 ml solution of potassium thiocyanate prepared at 10 mg/L (0.17mM) SCN$^-$ was prepared in a 0.01M NaOH matrix in a 250 ml Erlenmeyer flask. The initial concentration of cyanide, $T=0$, was measured to be zero. Once the starting concentration was determined, the flask was placed atop a stir-plate with a stir-bar and stirred gently. To the solution a 0.0203g dose of solid potassium ferrate was added. The solution produced a deep violet color that remained throughout the experiment. One minute after the addition, the first reading was measured. All readings that followed
occurred in 1min and 25sec intervals, a time equal to the delay time from sample draw to instrument reading. As figure 4.6 illustrates below, a sudden jump in detectable cyanide to where there was not one before was measured as the sulfur-cyanide bond was broken. The cyanide concentration fell gradually as it was oxidized to cyanate. The mixing of the sample and the analysis was allowed to continue until no change in cyanide concentration was detected, which corresponded to a total time of about 30 minutes. In this experiment the cyanide concentration did not drop below the 0.002mg/L detection limit of the instrument.

Figure 4.6 Production and Oxidation of Cyanide During Oxidation of Thiocyanate
The experiment with thiocyanate was repeated with a doubling of the potassium ferrate addition (0.0419g). In this experiment the cyanide concentration again failed to fall below the detection limit of the instrument. See figure 4.7.

**Figure 4.7 Production and Oxidation of Cyanide During Oxidation of Thiocyanate**

A third experiment was conducted with a second doubling of the potassium ferrate (0.0800g). Over the course of 53 minutes the cyanide produced by the oxidation of SCN⁻ ion fell below instrument detection.

A final experiment was repeated with the addition of 0.0800g potassium ferrate and allowed to react for one hour. Every five minutes for a total time of fifty minutes following ferrate addition a 5ml sample
was taken and quenched in an aliquot of 0.1N sodium arsenite to stop the oxidation process. At the 60
minute mark a final sample was taken and quenched in sodium arsenite. Thirteen samples were submitted
for analysis of the cyanate, thiocyanate, nitrite, nitrate, and other reduced sulfur species by Ion
Chromatography.

Figure 4.8 illustrates the brief formation of free cyanide as the thiocyanate bond is broken by ferrate
oxidation, and the subsequent oxidation of cyanide to cyanate. Figure 4.9 shows the determination of the
rate constant.

![Figure 4.8 Oxidation of Thiocyanate and Oxidation Products](image)
Figure 4.9  Rate Constant for the Oxidation of Thiocyanate by a 0.0800g dose of Potassium Ferrate

4.3  Copper (1) Cyanide as \([\text{Cu} (\text{CN})_3]^{2-}\)

A 100 ml solution of copper cyanide prepared at the specific ratio of 3:1 Cyanide to Copper was prepared at 10mg/L (0.0038M) as the CN\(^-\) ion in a 0.01M NaOH. The solution was transferred to a stirred 250 ml Erlenmeyer reaction flask. The initial concentration of cyanide, \(T=0\), measured at 10.4 mg/L (0.4mM). To the stirring solution a 0.0204g dose of solid potassium ferrate was added. The salt dissolved instantly and produced a deep violet color that instantly changed to an orange rust color. Eighty-five seconds after the ferrate was added, the cyanide was measured. Surprisingly 100% of the cyanide was oxidized to below instrument detection limit. The test was repeated and results were reproduced.

In order to determine the reaction rate, a series of low dose experiments were conducted on copper cyanide solutions again prepared to 10mg/L CN\(^-\) ion.

In the first experiment a 100 ml solution of 10 mg/L as the CN\(^-\) ion was prepared and transferred to a 250 ml Erlenmeyer reaction flask. The initial concentration, \(T=0\), measured at 10.27mg/L. To the stirring solution a 0.002g dose of solid potassium ferrate was added. The solution produced a deep violet color
that immediately diminished to an orange rust color. The subsequent reading showed an instant drop in cyanide concentration to 8.54mg/L.

A second solution was prepared and dosed with 0.004g potassium ferrate. The solution produced a deep violet color that immediately diminished to an orange rust color. Again, an instant drop in cyanide concentration was measured to 6.47mg/L.

A third solution was prepared and dosed with 0.006g potassium ferrate. The solution produced a deep violet color that immediately diminished to an orange rust color. Again, an instant drop in cyanide concentration was measured to 4.87mg/L.

A fourth solution was prepared and dosed with 0.008g potassium ferrate. The solution produced a deep violet color that immediately diminished to an orange rust color. Again, an instant drop in cyanide concentration was measured to 2.87mg/L.

And finally a fifth solution was prepared and dosed with 0.010g potassium ferrate. The solution produced a deep violet color that immediately diminished to an orange rust color. Again, an instant drop in cyanide concentration was measured to 1.21mg/L.

Table 4.1 Oxidation of copper cyanide relative to weight of potassium ferrate addition

<table>
<thead>
<tr>
<th>Potassium Ferrate</th>
<th>2.0 mg</th>
<th>4.0 mg</th>
<th>6.0 mg</th>
<th>8.0 mg</th>
<th>10.0 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) [CN] mg/L $T_o$</td>
<td>10.27</td>
<td>10.1</td>
<td>10.26</td>
<td>10.05</td>
<td>10.15</td>
</tr>
<tr>
<td>2) [CN] mg/L $T_f$</td>
<td>8.54</td>
<td>6.47</td>
<td>4.87</td>
<td>2.87</td>
<td>1.21</td>
</tr>
<tr>
<td>3) [CN] oxidized</td>
<td>1.73</td>
<td>3.63</td>
<td>5.39</td>
<td>7.18</td>
<td>8.94</td>
</tr>
<tr>
<td>4) [CN] oxidized per 2.0 mg</td>
<td>1.9</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td></td>
</tr>
</tbody>
</table>

The oxidation of copper cyanide, specifically the species at a 3:1 ratio $[\text{Cu(CN)}_3]^2-$, showed extremely rapid oxidation upon contact with potassium ferrate. Table 4.1 shows the results of five experiments where the dose of potassium ferrate is increased incrementally by 2.0 mg. Each 2.0 mg jump in dosage resulted in an additional 1.8 mg/L of cyanide oxidized as is shown in row four.
Due to the linear relationship, \( r^2 = 0.9998 \), between ferrate dose and the oxidation of copper cyanide, it is clear that the reaction rate remains constant regardless of amount of ferrate added. Because of this, zero-order kinetics is assumed.

\[
[C] = -kt + [C]_0
\]

Using the final results of each 2.0mg dose as shown in rows two and three, a rate constant was calculated using zero order kinetics and is shown in figure 4.10.

**Figure 4.10  Oxidation of Cyanide with Increasing Dosage of Potassium Ferrate**

4.3.1. **Copper Cyanide as \([Cu(CN)_3]\)\(^2\) as a Catalyst for Free Cyanide Oxidation**

Given the surprising results for the oxidation of copper cyanide, an experiment was done to determine if the rapid rate of oxidation is due to a catalytic effect by copper. Therefore the oxidation of free cyanide was repeated. Shown again for reference, figure 4.11, is the graph of the oxidation of free cyanide with a 0.0122g dosage of potassium ferrate. In the previous experiment the low dosage was not sufficient enough to oxidize cyanide to below the detection of the instrument. The test was repeated, but instead of allowing the reaction to go unabated, a 1.0 ml aliquot of 10mg/L CN as copper cyanide was
added after the eighty-five second measurement. The following reading at 170 seconds measured no cyanide. Complete oxidation of cyanide was achieved upon contact proving the catalytic nature of $[\text{Cu(CN)}_3]^2$.

Figure 4.11 Cyanide Oxidation With and Without Copper Cyanide Addition
4.4 Silver Cyanide as [Ag(CN)₂⁻]

In this experiment a 100 ml solution of silver cyanide made at 10 mg/L as cyanide was prepared in 0.01M NaOH and transferred to a 250 ml Erlenmeyer reaction flask. The initial concentration, T=0, measured at 9.99mg/L. To the stirring solution a 0.0200g dose of solid potassium ferrate was added. The solution produced a deep violet color that remained throughout the experiment. An apparent drop in cyanide was measured following ferrate addition. The measurement indicated an instant drop in cyanide concentration, but, after stabilizing at about 5.9 mg/L, the cyanide began to climb to previous levels.

The test was repeated with a 0.0515g dose of solid potassium ferrate. Again the cyanide measured a sharp drop to about 5mg/L, followed by a reversal as the concentration began to climb to previous levels. See figure 4.12.

**Figure 4.12 Oxidation of Silver Cyanide by Potassium Ferrate**

Interestingly, silver cyanide is considered to be a WAD cyanide species which means that it will dissociate into free cyanide ions in a weak acid. It showed an unusual resistance to oxidation by ferrate. This is not yet understood.
4.4.1 Copper Cyanide as \([\text{Cu(CN)}_3]^2\) as a Catalyst for Silver Cyanide Oxidation

An experiment was conducted in an attempt to test the catalytic effect of copper cyanide that was observed with free cyanide oxidation. A 10 mg/L solution of cyanide as silver cyanide was mixed with 10 mg/L cyanide as copper cyanide. An initial concentration of 19.6 mg/L was measured. A 0.0200g dose of potassium ferrate was added and the reaction measured. The results are shown in Figure 4.13.

An initial drop of 15 mg/L occurred in the first eighty-five seconds of the reaction followed by a stabilization of the cyanide level to just under 4mg/L. This development was puzzling since the color of the ferrate solution remained violet indicating an excess of unconsumed ferrate ion. Unfortunately the concentration did not fall to below detection as would be desired, but the cyanide level stayed constant indicating a reduction in the oxidative resistance of silver cyanide.

![Figure 4.13](image)

**Figure 4.13** Copper Catalytic Oxidation of Silver Cyanide by Potassium Ferrate

4.5 Nickel Cyanide as \([\text{Ni(CN)}_4]^2\)

Nickel Cyanide too showed an unusual resistance to oxidation by ferrate. A 100 ml solution of Nickel Cyanide prepared at 10 mg/L as the CN\(^-\) ion was prepared and transferred to a 250 ml Erlenmeyer
reaction flask. The initial concentration of cyanide, $T=0$, measured at 9.4 mg/L (0.36mM). To the stirring solution a 0.0200g dose of solid potassium ferrate was added. The salt dissolved instantly and produced a deep violet color that persisted throughout the experiment. Eighty-five seconds after ferrate addition, the first reading was measured. All readings that followed occurred in eighty-five second intervals. After an instant drop in measurable cyanide concentration a stabilization of the concentration occurred, even though a deep violet color persisted indicating an excess of the ferrate ion. See figure 4.14.

![Figure 4.14 Oxidation of Nickel Cyanide by Potassium Ferrate](image)

**Figure 4.14 Oxidation of Nickel Cyanide by Potassium Ferrate**

To determine a rate constant, an experiment for nickel cyanide was done in similar fashion to copper cyanide. Six solutions of 10mg/L cyanide as nickel cyanide were treated with increasing dosages (10 mg) of potassium ferrate. The reactions were stopped at the 10 minute mark by a quenching with sodium
arsenite. Ligand Exchange Reagent (see appendix D) was added and the remaining cyanide measured. The results are shown in table 4.2. The third row shows the total concentration of cyanide oxidized per 10mg dose.

<table>
<thead>
<tr>
<th>[CN] mg/L $T_o$</th>
<th>10.08</th>
<th>10.08</th>
<th>10.08</th>
<th>10.08</th>
<th>10.08</th>
<th>10.08</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CN] mg/L $T_f$</td>
<td>3.8</td>
<td>3.36</td>
<td>2.75</td>
<td>1.75</td>
<td>1.16</td>
<td>0.75</td>
</tr>
<tr>
<td>[CN] oxidized</td>
<td>6.28</td>
<td>6.72</td>
<td>7.33</td>
<td>8.33</td>
<td>8.92</td>
<td>9.33</td>
</tr>
</tbody>
</table>

As can be seen, a slightly higher rate of oxidation resulted from a higher dose, but again there was stabilization in concentration even with excess ferrate in solution as indicated by the deep purple color that persisted.

An experiment was conducted to determine if the addition of copper cyanide would have a catalytic effect with Nickel. The results were negative.

### 4.6 Cyanide Leach Tails from Newmont’s Phoenix Operation

Upon receiving the sample in the laboratory initial measurements of pH and temperature were recorded. Being about 60% solids the sample was separated into a dark, dense cake at the bottom and a clear solution at the top of the bottle. The sample was stirred with an impeller until homogenous. A 100ml aliquot of the slurry was taken and allowed to settle for about ten minutes. The clarified solution was filtered and submitted to the analytical laboratory for full characterization of dissolved metals, ions, and cyanide species. The settled solids were not characterized, but disposed of.

#### 4.6.1 Cyanide Leach Tails Slurry Detox

In this experiment a 500kg solution of leach tails slurry at 40% solids was weighed in a 1000ml plastic beaker. The slurry was mixed continuously with an impeller to maintain homogeneity. The stirring mixture was reacted with potassium ferrate in 100 mg doses. After each dose for a total of five doses, a 10
ml sample was taken. Reaction time for each dose was under 30 seconds. After the fifth addition, a final 500mg dose was added and a final sample taken. All six samples were allowed to settle and the clarified solution was filtered and submitted to NMS analytical for characterization of anions and cyanide species. Results are shown in table 4.3 and the results are graphed figures 4.15, 4.16, and 4.17.

Table 4.3 Characterization of Leach Slurry Before and After Ferrate Addition

<table>
<thead>
<tr>
<th></th>
<th>WAD</th>
<th>OCN</th>
<th>S2O3</th>
<th>S4O6</th>
<th>SCN</th>
<th>SO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C]o</td>
<td>22.6</td>
<td>8.13</td>
<td>518</td>
<td>25</td>
<td>447</td>
<td>1570</td>
</tr>
<tr>
<td>0.10 g</td>
<td>6.28</td>
<td>15.54</td>
<td>502</td>
<td>17.3</td>
<td>451</td>
<td>1610</td>
</tr>
<tr>
<td>0.20 g</td>
<td>0.93</td>
<td>17.51</td>
<td>479</td>
<td>10.9</td>
<td>450</td>
<td>1680</td>
</tr>
<tr>
<td>0.30 g</td>
<td>0.24</td>
<td>18.3</td>
<td>436</td>
<td>10.5</td>
<td>450</td>
<td>1760</td>
</tr>
<tr>
<td>0.40 g</td>
<td>0.09</td>
<td>18.98</td>
<td>396</td>
<td>9.3</td>
<td>456</td>
<td>1810</td>
</tr>
<tr>
<td>0.50 g</td>
<td>0.06</td>
<td>19.79</td>
<td>360</td>
<td>6.5</td>
<td>462</td>
<td>1840</td>
</tr>
<tr>
<td>1.00 g</td>
<td>0.03</td>
<td>23.63</td>
<td>168</td>
<td>1.3</td>
<td>460</td>
<td>2090</td>
</tr>
</tbody>
</table>

Figure 4.15 Leach Slurry Oxidation WAD Cyanide, Cyanide, and Tetrathionate

Figure 4.14 shows that full oxidation of WAD cyanide to cyanate was achieved following the third 100mg addition. Ferrate oxidation was also measured on tetrathionate, one of common reduced sulfur species present in cyanide leachates. Of additional interest is the fact that cyanate did not oxidize to nitrite.
and nitrate, both strictly regulated discharge parameters, and a problematic product in Caro’s Acid detox reactors.

**Figure 4.16 Leach Slurry Oxidation: Thiocyanate and Thiosulfate**

Figure 4-15 shows the ferrate oxidation of thiosulfate, a common reduced sulfur specie present in cyanide leachates. Interestingly, there was not a loss of ferrate to thiocyanate oxidation. This is understandable given the slow rate constant calculated in figure 4.8. The fact that thiocyanate remained untouched is beneficial with regards to reagent consumption, a serious problem in Caro’s Acid detox reactors.

And finally, in figure 4.16 the increase in sulfate is due to the oxidation of thiosulfate and tetrathionate.
Figure 4.17 Leach Slurry Oxidation: Sulfate
CHAPTER 5

CONCLUSIONS

5.1 Results on Synthetic Solutions

From the experiments conducted, some general conclusions can be made. First, the cyanide ion, free or complex, has shown acceptable response to oxidation by ferrate iron. Potassium Ferrate showed long term stability in high pH solutions which lends itself as an ideal candidate for use in lime/cyanide leaching systems. The slow oxidation rate of thiocyanate to form cyanate and the sulfate ion was calculated to be 0.03mg L$^{-1}$ min$^{-1}$. This is fortunate as it suggests the potential selectivity of ferrate iron relative to Caro’s Acid. It has also been shown that cyanate does not hydrolyze to ammonia as is seen in SO2/Air detox reactions, an observation that increases its potential as an alternative reagent.

The adequate, yet lower oxidation of nickel cyanide will need to be studied further. Although the nickel in a real world sample is less 1mg/L in most instances for Newmont leach tails, and is not a large contributor to the total cyanide levels in leach tails, the mere resistance could be problematic in a situation where the solution is to be discharged to the environment.

The discovery made regarding the catalytic oxidation via copper as copper cyanide is of extreme benefit in the regard that, all Newmont Properties where cyanide detoxification is utilized, copper cyanide is ubiquitous. There is no literature available for the oxidation of copper cyanides as could be cited, but instead a theory of the mechanism is proposed in figure 5.1.

The initial oxidation of [Cu(CN)$_3$]$_2^-$ by the ferrate ion produces the copper (II) ion that begins a three step catalytic process. In step one copper (II) is reduced back to copper (I) with the formation of CuCN and cyanogen gas. In step two the cyanogen oxidizes in an alkaline environment to form cyanate and the cyanide ion. In step three the CuCN then reacts with cyanide formed to reproduce [Cu(CN)$_3$]$_2^-$ and with excess ferrate the reaction repeats.
Figure 5.1 Illustration of Copper Cyanide Cycle

Step 1) \[ 2Cu^{2+} + 4CN^- \rightarrow 2CuCN + (CN)_2 \]

Step 2) \[ (CN)_2 + 2OH^- \rightarrow OCN^- + CN^- + H_2O \]

Step 3) \[ 2CuCN + 4CN^- \rightarrow 2[Cu(CN)_3]^{2-} \]

Overall Reaction
\[ 2Cu^{2+} + 7CN^- + 2OH^- \rightarrow OCN^- + 2[Cu(CN)_3]^{2-} \]
5.2 Results on Phoenix Leach Tails

The successful use of ferrate for the oxidation of cyanide species in the synthetic solutions led to an equally successful test on the Phoenix leach tails. Regardless of the pulp density (60% Solids) and the amount of oxidizeable species in solution, ferrate iron seemingly oxidized the cyanide species with very little trouble, no doubt aided by the presence of copper cyanide. By the fourth 100 mg dose, equivalent to about three minutes of reaction time, the WAD cyanide was below instrument detection and the thiocyanate level did not change suggesting a degree of selectivity. Such selectivity for cyanide is beneficial with regards to reagent consumption and the sludge volume produced from treatment.

5.3 Economic Considerations

Treatment of cyanide waste with an electrochemically produced potassium ferrate is not economically feasible (~$2.50/gram via Sigma Aldrich). The only other option is using an inline ferrate reactor proved by Ferrate Treatment Technologies, of Orlando Florida. Since the only two reagents required are very cheap, relative to ammonium bisulfite, they claim the operating costs to be as low as $0.05/1000 gal/ppm of ferrate.

Relative to the operating expenditure of Caro’s Acid and SO2/Air as shown in tables 2.1 and 2.2, minus labor and power consumption, ferrate treatment would be significantly cheaper. See table 5.1.

<table>
<thead>
<tr>
<th></th>
<th>$/m³</th>
<th>$/hr</th>
<th>$/day</th>
<th>$/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caro’s</td>
<td>0.227</td>
<td>238.35</td>
<td>5720</td>
<td>2,087,946</td>
</tr>
<tr>
<td>SO2/Air</td>
<td>0.248</td>
<td>260.4</td>
<td>6249.6</td>
<td>2,281,104</td>
</tr>
<tr>
<td>Ferrate</td>
<td>0.013</td>
<td>13.64</td>
<td>327.6</td>
<td>119,574</td>
</tr>
</tbody>
</table>
Preliminary reports from the manufacturer warn that ferrate production via oxidation of liquid ferric chloride will only produce a 2-4% ferrate concentration in solution and performing detox on slurries is not viable and the costs would undoubtedly rise significantly.

### 5.4 Suggestions for Future Research

A better understanding of the chemistry involved in the oxidation of nickel cyanide will be of importance in environmental applications. It may be of benefit to test the oxidation of nickel cyanide with the addition of copper cyanide to harness the apparent catalytic properties shown in this study. Also, since the oxidation potential of ferrate iron increases with a decrease in pH, testing nickel cyanide oxidation at lower pH ranges could return interesting results.

A deeper investigation into the mechanism behind the catalytic effect of copper cyanide would open it up to other applications beyond potassium ferrate. Some questions already being asked are: 1) How would copper cyanide behave in the SO₂/Air process in place of copper sulfate which already is a known catalyst for the reaction? And 2) Can Caro’s Acid benefit from a catalyst and if so, will copper cyanide improve selectivity.

Since the production of an electrolytically pure potassium ferrate is not of economic value without a source of cheap energy, the testing of a ferrate generator offered by Ferrate Treatment Technologies will commence in 2013 to determine if inline injection of ferrate is effective. Preliminary reports from the manufacturer warn that ferrate production via oxidation of liquid ferric chloride will only produce a 2-4% ferrate concentration in solution and performing detox on clarified solutions is not viable.
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58


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APPENDIX A

EXPERIMENTAL DATA – GAS DIFFUSION AMPEROMETRY OF $C_{N_{\text{wad}}}$
### Table A-1 Oxidation of Free Cyanide

0.0122g K$_2$FeO$_4$ to 100 ml of 10mg/L CN-

<table>
<thead>
<tr>
<th>Peak</th>
<th>Time(s)</th>
<th>Cup</th>
<th>Name</th>
<th>Dilution</th>
<th>Response (pA)</th>
<th>CN- mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>105</td>
<td>Sync</td>
<td>1</td>
<td>1642649</td>
<td>10.04</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>105</td>
<td>Sync</td>
<td>1</td>
<td>1649306</td>
<td>10.08</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>105</td>
<td>Sync</td>
<td>1</td>
<td>1675111</td>
<td>10.24</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>101</td>
<td>blank</td>
<td>1</td>
<td>2980</td>
<td>-0.06</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>101</td>
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### Table A-6 Oxidation of Silver Cyanide with Copper Addition

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APPENDIX B

EXPERIMENTAL DATA – ION CHROMATOGRAPHY
### Table B-1 Cyanate by IC

**OCN Formation of Free Cyanide Oxidation**

0.0199g K2FeO4 to 100 ml of 10mg/L CN-

Ion Chromatography

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<thead>
<tr>
<th>NM-214423</th>
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### Table B-2 Anions by IC

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<td>NaAsO2</td>
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<td>SCN 10mg/L</td>
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<td>t5</td>
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APPENDIX C

EXPERIMENTAL DATA – LEACH TAILS CHARACTERIZATION AND DETOX
### Table C-1  Leach Tails Characterization by IC

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### Table C-2  Leach Tail Characterization by Gas Diffusion Amperometry

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APPENDIX D

OIA-METHOD 1677
Method OIA-1677
Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry
Acknowledgments

This method was developed by Michael Straka of OI Analytical in cooperation with Emil Milosavljevic and Ljiljana Solujic of the University of Nevada Reno Mackay School of Mines and guidance from William A. Telliard of the Engineering and Analysis Division (EAD) within the U.S. Environmental Protection Agency’s (EPA’s) Office of Science and Technology (OST). Additional assistance in preparing the method was provided by DynCorp Information and Enterprise Technology and Interface, Inc..

Disclaimer

This Method has been reviewed and approved for publication by the Analytical Methods Staff within EPA’s Engineering and Analysis Division. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Questions concerning this Method or its application should be addressed to:

W.A. Telliard
Engineering and Analysis Division (4303)
U.S. Environmental Protection Agency
401 M Street SW
Washington, DC 20460
Phone: 202/260–7120
Fax: 202/260–7185
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Introduction

Method OIA-1677 was developed by ALPKEM, a division of OI Analytical, in cooperation with the University of Nevada Reno Mackay School of Mines, as a way to measure available cyanide without the interference problems of the currently approved available cyanide methods. EPA proposed the use of Method OIA-1677 on July 7, 1998 (63 FR 36809). EPA is approving the use of Method OIA-1677 for compliance monitoring under Section 304(h) of the Clean Water Act. Method OIA-1677 is an additional test procedure for measuring the same cyanide species as are measured by currently approved methods for cyanide amenable to chlorination (CATC). In some matrices, CATC methods are subject to significant test interferences. Method OIA-1677 has been added to the list of approved methods because it is more specific for available cyanide, is more rapid, measures cyanide at lower concentrations, offers improved safety, reduces laboratory waste, and is more precise and accurate than currently approved CATC methods.

Requests for additional copies of this Method should be directed to:

Attn: Catherine Anderson
ALPKEM
A Division of OI Analytical
PO Box 9010
College Station, TX 77842-9010
Phone: 409/690-1711
Fax: 409/690-0440

National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161
Phone: 800/553-6847 or 703/605-6000
PB99-132011
Note: This Method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this Method are met. The laboratory may not omit any quality control tests. The terms "shall" and "must" define procedures required for producing reliable data at water quality criteria levels. The terms "should" and "may" indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces results equivalent or superior to results produced by this Method.
**Method OIA-1677**

**Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry**

1.0 **Scope and Application**

1.1 This method is for determination of available cyanide in water and wastewater by flow injection, ligand exchange, and amperometric detection. The method is for use in EPA’s data gathering and monitoring programs associated with the Clean Water Act, Resource Conservation and Recovery Act, Comprehensive Environmental Response, Compensation and Liability Act, and Safe Drinking Water Act.

1.2 Cyanide ion (CN⁻), hydrogen cyanide in water (HCNₐq), and the cyano-complexes of zinc, copper, cadmium, mercury, nickel, and silver may be determined by this method (see Section 17.2.1).

1.3 The presence of polysulfides may prove intractable for application of this method.

1.4 The method detection limit (MDL) is 0.5 µg/L and the minimum level (ML) is 2.0 µg/L. The dynamic range is approximately 2.0 µg/L (ppb) to 5.0 mg/L (mg/L) cyanide ion using a 200 µL sample loop volume. Higher concentrations can be determined by dilution of the original sample or by reducing volume of the sample loop.

1.5 This method is for use by analysts experienced with flow injection equipment or under close supervision of such qualified persons.

1.6 The laboratory is permitted to modify the method to overcome interferences or to lower the cost of measurements, provided that all performance criteria in this method are met. Requirements for establishing method equivalency are given in Section 9.1.2.

2.0 **Summary of Method**

2.1 The analytical procedure employed for determination of available cyanide is divided into two parts: sample pretreatment and cyanide detection. In the pretreatment step, ligand-exchange reagents are added at room temperature to 100 mL of a cyanide-containing sample. The ligand-exchange reagents form thermodynamically stable complexes with the transition metal ions listed in Section 1.2, resulting in the release of cyanide ion from the metal-cyano complexes.

Cyanide detection is accomplished using a flow-injection analysis (FIA) system (Reference 15.6). A 200-µL aliquot of the pre-treated sample is injected into the flow injection manifold of the system. The addition of hydrochloric acid converts cyanide ion to hydrogen cyanide (HCN) that passes under a gas diffusion membrane. The HCN diffuses through the membrane into an alkaline receiving solution where it is converted back to cyanide ion. The cyanide ion is monitored amperometrically with a silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter...
electrode, at an applied potential of zero volt. The current generated is proportional to the cyanide concentration present in the original sample. Total analysis time is approximately two minutes.

2.2 The quality of the analysis is assured through reproducible calibration and testing of the FIA system.

2.3 A flow diagram of the FIA system is shown in Figure 1.

![Flow injection Manifold](image)

**Figure 1.** Flow injection Manifold used in the quantification of cyanide in the pretreated sample. Carrier (0.1 M HCl); Acid (0.1 M HCl); Acceptor (0.1 M NaOH).

3.0 **Definitions**

Definitions for terms used in this method are given in the glossary at the end of the method.

4.0 **Interferences**

4.1 Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts that affect results. Specific selection of reagents or purification of these reagents may be required.

4.2 All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running laboratory blanks as described in Section 9.4.

4.3 Glassware is cleaned by washing in hot water containing detergent, rinsing with tap and reagent water, and drying in an area free from interferences.

4.4 Interferences extracted from samples will vary considerably from source to source, depending upon the diversity of the site being sampled.

4.5 Sulfide is a positive interferent in this method (References 15.3 and 15.4), because an acidified sample containing sulfide liberates hydrogen sulfide that is passed through the
membrane and produces a signal at the silver electrode. In addition, sulfide ion reacts with cyanide ion in solution to reduce its concentration over time. To overcome this interference, the sulfide ion must be precipitated with lead ion immediately upon sample collection. Sulfide ion and lead sulfide react with cyanide ion to form thiocyanate which is not detected in the analytical system. Tests have shown (Reference 15.7) that if lead carbonate is used for sulfide precipitation, the supernate containing cyanide must be filtered immediately to avoid loss of cyanide through reaction with precipitated lead sulfide (Section 8.2.1).

4.6 Though not interferences, substances that react with cyanide should also be removed from samples at time of collection. These substances include water soluble aldehydes that form cyanohydrins and oxidants such as hypochlorite and sulfite. Water soluble aldehydes react with cyanide to form cyanohydrins that are not detected by the analytical system; hypochlorite and sulfite oxidize cyanide to non-volatile forms. Procedures for the removal of these substances are provided in Sections 8.2.2 and 8.2.3.

5.0 Safety

5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.2 Cyanides and cyanide solutions

WARNING: The cyanide ion, hydrocyanic acid, all cyanide salts, and most metal-cyanide complexes are extremely dangerous. As a contact poison, cyanide need not be ingested to produce toxicity. Also, cyanide solutions produce fatally toxic hydrogen cyanide gas when acidified. For these reasons, it is mandatory that work with cyanide be carried out in a well-ventilated hood by properly trained personnel wearing adequate protective equipment.

5.3 Sodium hydroxide solutions

CAUTION: Considerable heat is generated upon dissolution of sodium hydroxide in water. It may be advisable to cool the container in an ice bath when preparing sodium hydroxide solutions.

5.4 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

5.5 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 15.8 and 15.9.
6.0 Equipment and Supplies

NOTE: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 Flow injection analysis (FIA) system—ALPKEM Model 3000 (Reference 15.5), or equivalent, consisting of the following:

6.1.1 Injection valve capable of injecting 40 to 300 μL samples

6.1.2 Gas diffusion manifold with a microporous Teflon® or polypropylene membrane

6.1.3 Amperometric detection system with:

   6.1.3.1 Silver working electrode

   6.1.3.2 Ag/AgCl reference electrode

   6.1.3.3 Pt/stainless steel counter electrode

   6.1.3.4 Applied potential of 0.0 volt

6.2 Sampling equipment—Sample bottle, amber glass, 0.1-L, with polytetrafluoroethylene (PTFE)-lined cap. Clean by washing with detergent and water, rinsing with two aliquots of reagent water, and drying by baking at 110 - 150 °C for one hour minimum.

6.3 Standard laboratory equipment including volumetric flasks, pipettes, syringes, etc. all cleaned, rinsed and dried per bottle cleaning procedure in Section 6.2.

7.0 Reagents and Standards

7.1 Reagent water—Water in which cyanide and potentially interfering substances are not detected at the MDL of this method. It may be generated by any one of the methods listed below. Reagent water generated by these methods shall be tested for purity utilizing the procedure in Section 11.

   7.1.1 Activated carbon—Pass distilled or deionized water through an activated carbon bed (Calgon Filtrasorb-300 or equivalent).

   7.1.2 Water purifier—Pass distilled or deionized water through a purifier (Millipore Super Q, or equivalent).

7.2 Sodium hydroxide—ACS reagent grade.

7.3 Potassium cyanide—ACS reagent grade.
7.4 Mercury (II) cyanide, ≥99% purity—Aldrich Chemical Company Catalog No. 208140, or equivalent.

7.5 Potassium nickel (II) cyanide—Aldrich Chemical Company Catalog No. 415154, or equivalent.

7.6 Silver nitrate—ACS reagent grade. Aldrich Chemical Company Catalog No. 209139, or equivalent.

7.7 Hydrochloric acid—approximately 37%, ACS reagent grade.

7.8 Preparation of stock solutions. Observe the warning in Section 5.2.

7.8.1 Silver nitrate solution, 0.0192 N—Weigh 3.27 g of AgNO₃ into a 1-L volumetric flask and bring to the mark with reagent water.

7.8.2 Rhodanine solution, 0.2 mg/mL in acetone—Weigh 20 mg of p-dimethylaminobenzalrhodanine (Aldrich Chemical Co. Catalog No. 114588, or equivalent) in a 100-mL volumetric flask and dilute to the mark with acetone.

7.8.3 Potassium cyanide stock solution, 1000 mg/L

7.8.3.1 Dissolve approximately 2 g (approximately 20 pellets) of sodium hydroxide in approximately 500 mL of reagent water contained in a one liter volumetric flask. Observe the caution in Section 5.3. Add 2.51 g of potassium cyanide (Aldrich Chemical Co. Catalog No. 207810, or equivalent), dilute to one liter with reagent water, and mix well. Store KCN solution in an amber glass container at 0-4°C.

7.8.3.2 Standardize the KCN solution (Section 7.8.3.1) by adding 0.5 mL of rhodanine solution (Section 7.8.2) to 25 mL of KCN solution and titrating with AgNO₃ solution (Section 7.8.1) until the color changes from canary yellow to a salmon hue. Based on the determined KCN concentration, dilute the KCN solution to an appropriate volume so the final concentration is 1.00 g/L, using the following equation:
EQUATION 1

\[ x \times v = 1 \text{ g/L} \times 1 \text{ L} \]

where:
\( x = \text{concentration of KCN solution determined from titrations} \)
\( v = \text{volume of KCN solution needed to prepare 1 L of 1 g/L KCN solution} \)

If the concentration is not 1.00 g/L, correct the intermediate and working calibration concentrations accordingly.

7.8.4 1M sodium hydroxide—Dissolve 40 g of sodium hydroxide pellets in approximately 500 mL of reagent water in a 1-liter volumetric flask, observing the caution in Section 5.3. Dilute to one liter with reagent water. Store in an amber bottle at room temperature.

7.9 Secondary standards.

7.9.1 Cyanide, 100 mg/L—Dilute 100.0 mL of cyanide stock solution (Section 7.8.3.2) and 10 mL of 1M sodium hydroxide (Section 7.8.4) to one liter with reagent water (Section 7.1). Store in an amber glass bottle at 0-4°C.

7.9.2 Cyanide, 10 mg/L—Dilute 10.0 mL of cyanide stock solution and 10 mL of 1M sodium hydroxide to one liter with reagent water. Store in an amber glass bottle at 0-4°C.

7.9.3 Cyanide, 1 mg/L—Dilute 1.0 mL of cyanide stock solution and 1 mL of 1M sodium hydroxide to one liter with reagent water. Store in an amber glass bottle at 0-4°C.

7.9.4 Cyanide working calibration standard solutions (2 - 5000 μg/L as cyanide)—Working calibration standards may be prepared to cover the desired calibration range by adding the appropriate volumes of secondary standards (Sections 7.9.1, 7.9.2, 7.9.3) to 100 mL volumetric flasks that contain 40 mL of reagent water (Section 7.1) and 1 mL of 1M sodium hydroxide (Section 7.8.4). Dilute the solutions to 100 mL with reagent water. Prepare working calibration standards daily. The following table provides the quantity of secondary standard necessary to prepare working standards of the specified concentration.
### Method OIA-1677

<table>
<thead>
<tr>
<th>Working Calibration Standard Concentration (μg/L)</th>
<th>Secondary Standard Solution Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Secondary Standard Concentration (Section 7.8.3)</td>
</tr>
<tr>
<td></td>
<td>1 mg/L</td>
</tr>
<tr>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.200</td>
</tr>
<tr>
<td>5.0</td>
<td>0.500</td>
</tr>
<tr>
<td>10.0</td>
<td>1.00</td>
</tr>
<tr>
<td>50.0</td>
<td>5.00</td>
</tr>
<tr>
<td>100</td>
<td>10.0</td>
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<tr>
<td>200</td>
<td>20.0</td>
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<tr>
<td>500</td>
<td>50.0</td>
</tr>
<tr>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td></td>
</tr>
</tbody>
</table>

If desired, the laboratory may extend the analytical working range by using standards that cover more than one calibration range, so long as the requirements of Section 10.3 are met.

### 7.10 Sample Preservation Reagents

7.10.1 The presence of sulfide may result in the conversion of cyanide to thiocyanate. While lead acetate test paper has been recommended for determining the presence of sulfide in samples, the test is generally unreliable and is typically not usable for sulfide concentrations below approximately 1 mg/L. The use of lead carbonate (Aldrich Chemical Co. Catalog No. 336378, or equivalent), followed by immediate filtration of the sample is required whenever sulfide ion is present. If the presence of sulfide is suspected but not verifiable from the use of lead acetate test paper, two samples may be collected, one without lead carbonate addition and another with lead carbonate addition followed by immediate filtration. Analyze both samples. If sulfide is present, the preserved sample should contain higher levels of cyanide than the unpreserved sample. Lead acetate test paper may be used, but should be tested for minimum level of sulfide detection by spiking reagent water aliquots with decreasing levels of sulfide and determining the lowest level of sulfide detection attainable. The spiked samples are tested with lead acetate test paper moistened with acetate buffer solution. The buffer solution is prepared by
dissolving 146 g anhydrous sodium acetate, or 243 g sodium acetate trihydrate in 400 mL of reagent water, followed by addition of 480 g concentrated acetic acid. Dilute the solution to 1 L with reagent water. Each new batch of test paper and/or acetate buffer should be tested to determine the lowest level of sulfide ion detection prior to use.

7.10.2 Ethylenediamine solution—In a 100 mL volumetric flask, dilute 3.5 mL pharmaceutical-grade anhydrous ethylenediamine (Aldrich Chemical Co. Catalog No. 240729, or equivalent) with reagent water.

7.10.3 Ascorbic acid—Crystals—Aldrich Chemical Co. Catalog No. 268550, or equivalent.

7.11 FIA Reagents.

7.11.1 Carrier and acid reagent (0.1M hydrochloric acid)—Dilute 8 mL of concentrated hydrochloric acid to one liter with reagent water.

7.11.2 Acceptor reagent (0.1M sodium hydroxide)—Dilute 100 mL of sodium hydroxide solution (Section 7.8.4) to 1000 mL with reagent water.

7.11.3 Ligand-exchange reagent A-ALPKEM part number A001416, or equivalent.

7.11.4 Ligand-exchange reagent B-ALPKEM part number A001417, or equivalent.

7.12 Quality control solutions

7.12.1 Mercury (II) cyanide stock solution (1000 mg/L as cyanide)—Weigh 0.486 g of mercury (II) cyanide (Section 7.4) in a 100-mL volumetric flask. Add 10 - 20 mL of reagent water and 1 mL of 1M sodium hydroxide solution (Section 7.8.4). Swirl to mix. Dilute to the mark with reagent water.

7.12.2 Laboratory control sample (LCS)—Place 0.20 mL of the mercury (II) cyanide stock solution (Section 7.12.1) in a 100-mL volumetric flask and dilute to the mark with reagent water to provide a final cyanide concentration of 2.00 mg/L.

8.0 Sample Collection, Preservation, and Storage

8.1 Sample collection and preservation—Samples are collected using manual (grab) techniques and are preserved immediately upon collection.

8.1.1 Grab sampling—Collect samples in amber glass bottles with PTFE-lined caps cleaned according to the procedure in Section 6.2. Immediately after collection, preserve the sample using any or all of the preservation techniques (Section 8.2), followed by adjustment of the sample pH to ≤12 by addition of 1M sodium hydroxide and refrigeration at 0-4°C.
8.1.2 Compositing—Compositing is performed by combining aliquots of grab samples only. Automated compositing equipment may not be used because cyanide may react or degrade during the sampling period. Preserve and refrigerate each grab sample immediately after collection (Sections 8.1.1 and 8.2) until compositing.

8.1.3 Shipment—If the sample will be shipped by common carrier or mail, limit the pH to a range of 12.0 - 12.3. (See the footnote to 40 CFR 136.3(e), Table II, for the column headed "Preservation.")

8.2 Preservation techniques

8.2.1 Samples containing sulfide ion

8.2.1.1 Test the sample with lead acetate test paper (Section 7.10.1) to determine the presence or absence of sulfide ion. If sulfide ion is present, the sample must be treated immediately (within 15 minutes of collection) with sufficient solid lead carbonate (Section 7.10.1) to remove sulfide (as evidenced by the lead acetate test paper), and immediately filtered into another sample bottle to remove precipitated lead sulfide.

8.2.1.2 If sulfide ion is suspected to be present, but its presence is not detected by the lead acetate paper test, two samples should be collected. One is treated for the presence of sulfide and immediately filtered, while the second is not treated for sulfide. Both samples must be analyzed. (Tests conducted prior to the interlaboratory validation of this method showed significant and rapid losses of cyanides when lead sulfide was allowed to remain in contact with the sample during holding times of three days or less. As a result, the immediate filtration of samples preserved with lead carbonate is essential (Reference 15.6)).

8.2.1.3 If the sample contains particulate matter that would be removed upon filtration, the sample must be filtered prior to treatment with lead carbonate to assure that cyanides associated with the particulate matter are included in the measurement. The collected particulate matter must be saved and the filtrate treated using the sulfide removal procedure above (Section 8.2.1.1). The collected particulate and treated filtrate must be recombined and homogenized, and then sent to the laboratory for analysis.

8.2.2 Samples containing water soluble aldehydes—Treat samples containing or suspected to contain formaldehyde, acetaldehyde, or other water soluble aldehydes with 20 mL of 3.5% ethylenediamine solution (Section 7.10.2) per liter of sample.

8.2.3 Samples known or suspected to contain chlorine, hypochlorite, and/or sulfite—Treat with 0.6 g of ascorbic acid (Section 7.10.3) per liter of sample. EPA Method 330.4 or 330.5 may be used for the measurement of residual chlorine (Reference 15.1).
8.3 Sample holding time—Maximum holding time for samples preserved as above is 14 days. Unpreserved samples must be analyzed within 24 hours, or sooner if a change in cyanide concentration will occur. (See the footnotes to Table II at 40 CFR 136.3(e).)

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 15.9). The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of LCSs and MS/MSDs as a continuing check on performance. Laboratory performance is compared to established performance criteria to determine if the results of the analyses meet the performance characteristics of the method.

9.1.1 The laboratory shall make an initial demonstration of the ability to generate acceptable precision and accuracy with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, and to allow the laboratory to overcome sample matrix interferences, the laboratory is permitted certain options to improve performance or lower the costs of measurements. Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, then that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analytes of interest.

9.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in Section 9.2. If the detection limit of the method will be affected by the change, the laboratory must demonstrate that the MDL is equal to or less than the MDL in Section 1.4 or one-third the regulatory compliance level, whichever is greater. If calibration will be affected by the change, the laboratory must recalibrate the instrument per Section 10.3.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the information in this subsection, at a minimum.

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modification.

9.1.2.2.2 A narrative stating the reason(s) for the modification.

9.1.2.2.3 Results from all quality control (QC) tests comparing the modified method to this method including:
(a) calibration (Section 10.3)
(b) calibration verification (Section 9.5)
(c) initial precision and recovery (Section 9.2)
(d) analysis of blanks (Section 9.4)
(e) laboratory control sample (Section 9.6)
(f) matrix spike and matrix spike duplicate (Section 9.3)
(g) MDL (Section 1.4)

9.1.2.2.4 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

(a) sample numbers and other identifiers
(b) analysis dates and times
(c) analysis sequence/run chronology
(d) sample weight or volume
(e) sample volume prior to each cleanup step, if applicable
(f) sample volume after each cleanup step, if applicable
(g) final sample volume prior to injection (Sections 10 and 11)
(h) injection volume (Sections 10 and 11)
(i) dilution data, differentiating between dilution of a sample or modified sample (Sections 10 and 11)
(j) instrument and operating conditions
(k) other operating conditions (temperature, flow rates, etc.)
(l) detector (operating condition, etc.)
(m) printer tapes, disks, and other recording of raw data
(n) quantitation reports, data system outputs, and other data necessary to link raw data to the results reported

9.1.3 Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in Section 9.3.

9.1.4 Analyses of blanks are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis. The procedures and criteria for analysis of a blank are described in Section 9.4.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through the analysis of the LCS (Section 7.12.2) that the analysis system is in control. This procedure is described in Section 9.6.
9.1.6 The laboratory should maintain records to define the quality of data that is generated. Development of accuracy statements is described in Sections 9.3.8 and 9.6.3.

9.1.7 Accompanying QC for the determination of cyanide is required per analytical batch. An analytical batch is a set of samples analyzed at the same time, to a maximum of 10 samples. Each analytical batch of 10 or fewer samples must be accompanied by a laboratory blank (Section 9.4), an LCS (Section 9.6), and a matrix spike and matrix spike duplicate (MS/MSD, Section 9.3), resulting in a minimum of five analyses (1 sample, 1 blank, 1 LCS, 1 MS, and 1 MSD) and a maximum of 14 analyses (10 samples, 1 blank, 1 LCS, 1 MS, and 1 MSD) in the batch. If greater than 10 samples are analyzed at one time, the samples must be separated into analytical batches of 10 or fewer samples.

9.2 Initial demonstration of laboratory capability

9.2.1 Method Detection Limit (MDL)—To establish the ability to detect cyanide at low levels, the laboratory shall determine the MDL per the procedure in 40 CFR Part 136, Appendix B (Reference 15.4) using the apparatus, reagents, and standards that will be used in the practice of this method. An MDL less than or equal to the MDL listed in Section 1.4 must be achieved prior to practice of this method.

9.2.2 Initial Precision and Recovery (IPR)—To establish the ability to generate acceptable precision and accuracy, the laboratory shall perform the following operations:

9.2.2.1 Analyze four samples of the LCS (Section 7.12.2) according to the procedure beginning in Section 10.

9.2.2.2 Using the results of the set of four analyses, compute the average percent recovery (x) and the standard deviation of the percent recovery (s) for cyanide. Use Equation 2 for calculation of the standard deviation of the percent recovery.

\[
\text{EQUATION 2}
\]

\[
s = \sqrt{\frac{x^2 - (\bar{x})^2}{n - 1}}
\]

\[
where:
\]

\[
n = \text{Number of samples}
\]

\[
x = \text{Percent recovery in each sample}
\]
9.2.3 Compare s and x with the acceptance criteria specified in Table 1. If s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable and the problem must be found and corrected before analyses can begin.

9.3 Matrix spike/matrix spike duplicate (MS/MSD)—The laboratory shall spike, in duplicate, a minimum of 10 percent of all samples (one sample in duplicate in each batch of ten samples) from a given discharge.

9.3.1 The concentration of the spike in the sample shall be determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of cyanide in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1 to 5 times higher than the background concentration of the sample (determined in Section 9.3.2), whichever concentration is higher.

9.3.1.2 If the concentration of cyanide in a sample is not being checked against a limit, the spike shall be at the concentration of the LCS or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

9.3.2 Analyze one sample aliquot out of each set of ten samples from each discharge according to the procedure beginning in Section 11 to determine the background concentration (B) of cyanide.

9.3.2.1 Spike this sample with the amount of mercury (II) cyanide stock solution (Section 7.12.1) necessary to produce a cyanide concentration in the sample of 2 mg/L. If necessary, prepare another stock solution appropriate to produce a level in the sample at the regulatory compliance limit or at 1 to 5 times the background concentration (per Section 9.3.1).

9.3.2.2 Spike two additional sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A).

9.3.3 Calculate the percent recovery of cyanide in each aliquot using Equation 3.
**Equation 3**

\[ p = \frac{100 \times (A - B)}{T} \]

where:

- \( p \) = Percent recovery
- \( A \) = Measured concentration of cyanide after spiking
- \( B \) = Measured background concentration of cyanide
- \( T \) = True concentration of the spike

9.3.4 Compare the recovery to the QC acceptance criteria in Table 1. If recovery is outside of the acceptance criteria, and the recovery of the LCS in the ongoing precision and recovery test (Section 9.6) for the analytical batch is within the acceptance criteria, an interference is present. In this case, the result may not be reported for regulatory compliance purposes.

9.3.5 If the results of both the MS/MSD and the LCS test fail the acceptance criteria, the analytical system is judged to be out of control. In this case, the problem shall be identified and corrected, and the analytical batch reanalyzed.

9.3.6 Calculate the relative percent difference (RPD) between the two spiked sample results (Section 9.3, not between the two percent recoveries) using Equation 4.

**Equation 4**

\[ RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100 \]

where:

- \( RPD \) = Relative percent difference
- \( D_1 \) = Concentration of cyanide in the spiked sample
- \( D_2 \) = Concentration of cyanide in the spiked duplicate sample

9.3.7 Compare the precision to the RPD criteria in Table 1. If the RPD is greater than the acceptance criteria, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch reanalyzed.

9.3.8 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained. After the analysis of five spiked samples in which the recovery passes the test in Section 9.3.4, compute the average percent recovery \( (P_a) \) and the standard deviation of the percent recovery \( (s_p) \). Express the accuracy assessment as a percent recovery.
interval from $P_a - 2s_p$ to $P_a + 2s_p$. For example, if $P_a = 90\%$ and $s_p = 10\%$ for five analyses, the accuracy interval is expressed as $70 - 110\%$. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).

9.4 Laboratory blanks—Laboratory reagent water blanks are analyzed to demonstrate freedom from contamination.

9.4.1 Analyze a reagent water blank initially (i.e., with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.4.2 If cyanide is detected in the blank at a concentration greater than the ML, analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination.

9.5 Calibration verification—Verify calibration of the analytical equipment before and after each analytical batch of 14 or fewer measurements. (The 14 measurements will normally be 10 samples, 1 reagent blank, 1 LCS, 1 MS, and 1 MSD). Verification is accomplished by analyzing the mid-range calibration standard and verifying that it is within the QC acceptance criteria for recovery in Table 1. (The concentration of the calibration verification depends on the calibration range being used.) Failure to verify calibration within the acceptance criteria requires recalibration of the analysis system.

9.6 Laboratory control sample (LCS)—To demonstrate that the analytical system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the laboratory shall perform the following operations.

9.6.1 Analyze a LCS (Section 7.12.2) with each analytical batch according to the procedure in Section 10.

9.6.2 If the results for the LCS are within the acceptance criteria specified in Table 1, analysis of the batch may continue. If, however, the concentration is not within this range, the analytical process is not in control. In this event, correct the problem, repeat the LCS test, and reanalyze the batch.

9.6.3 The laboratory should add results that pass the specification in Section 9.6.2 to IPR and previous LCS data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for cyanide by calculating the average percent recovery ($R$) and the standard deviation of the percent recovery ($s_r$). Express the accuracy as a recovery interval from $R - 2s_r$ to $R + 2s_r$. For example, if $R = 95\%$ and $s_r = 5\%$, the accuracy is $85\%$ to $105\%$.

9.7 Reference Sample—To demonstrate that the analytical system is in control, the laboratory should periodically test an external reference sample, such as a Standard Reference Material (SRM) if an SRM is available from the National Institutes of Standards and
Technology (NIST). The reference sample should be analyzed quarterly, at a minimum. Corrective action should be taken if the measured concentration significantly differs from the stated concentration.

10.0 Calibration and Standardization

This section describes the procedure to calibrate and standardize the FIA system prior to cyanide determination.

10.1 Instrument setup

10.1.1 Set up the FIA system and establish initial operating conditions necessary for determination of cyanide. If the FIA system is computerized, establish a method for multi-point calibration and for determining the cyanide concentration in each sample.

10.1.2 Verify that the reagents are flowing smoothly through the FIA system and that the flow cell is purged of air bubbles.

10.2 Instrument Stabilization

10.2.1 Load a 10 mg/L KCN standard (Section 7.8.3) into the sampling valve and inject into the FIA system.

10.2.2 Continue to inject 10 mg/L KCN standards until 3 successive peak height or area results are within 2% RSD, indicating that the electrode system is stabilized.

10.2.3 Following stabilization, inject the highest concentration calibration standard until 3 successive peak height or area results are within 2% RSD indicating stabilization at the top of the calibration range.

10.3 External standard calibration

10.3.1 Inject each of a minimum of 3 calibration standards. One of the standards should be at the minimum level (ML) unless measurements are to be made at higher levels. The other concentrations should correspond to the expected range of concentrations found in samples or should define the working range of the FIA system.

10.3.2 Using injections of a constant volume, analyze each calibration standard according to Section 11 and record peak height or area responses against the concentration. The results can be used to prepare a calibration curve. Alternatively, if the ratio of response to amount injected (calibration factor) is constant over the working range (<10% RSD), linearity through the origin can be assumed and the averaged calibration factor (area/concentration) can be used in place of a calibration curve.
11.0 Procedure

This section describes the procedure for determination of available cyanide using the FIA system.

11.1 Analysis of standards, samples, and blanks

11.1.1 Ligand-exchange reagent treatment of standards, samples, and blanks.

11.1.2 To 100-mL of cyanide-containing sample (or standard or blank) at pH of approximately 12, add 100 µL of ligand-exchange reagent Part B (Section 7.11.5), 50µL of ligand-exchange reagent Part A (Section 7.11.4), and mix thoroughly. Load the sample, standard, or blank into the sample loop.

NOTE: The ligand-exchange reagents, when added to 100 mL of sample at the specified volume, will liberate cyanide from metal complexes of intermediate stability up to 5 mg/L cyanide ion. If higher concentrations are anticipated, add additional ligand-exchange reagent, as appropriate, or dilute the sample. The ligand-exchange reagents have an approximate lifetime of 6 months after opening. The reagents should be stored in a refrigerator at 4°C. Samples should be analyzed within 2 hours of adding the ligand-exchange reagents. The reagents should always be used in solutions similar to cyanide samples (pH 12 adjusted). It is recommended that the ligands be checked monthly. This can be done by preparing pH 12 adjusted 2 mg/l solutions of mercury(II) cyanide (Section 7.4) and of potassium nickel(II) cyanide (Section 7.5). Add ligand-exchange reagent B to the mercury(II) standard and ligand-exchange reagent A to the potassium nickel(II) cyanide standard and confirm cyanide recovery.

11.1.3 Inject the sample and begin data collection. When data collection is complete, analyze the next sample, standard or blank in the batch until analyses of all samples in the batch are completed.

12.0 Data Analysis and Calculations

12.1 Calculate the concentration of material in the sample, standard or blank from the peak height or area using the calibration curve or calibration factor determined in Section 10.3.

12.2 Reporting

12.2.1 Samples—Report results to three significant figures for cyanide concentrations found above the ML (Section 1.4) in all samples. Report results below the ML as <2 µg/L, or as required by the permitting authority or permit.

12.2.2 Blanks—Report results to three significant figures for cyanide concentrations found above the MDL (Section 1.4). Do not report results below the MDL unless required by the permitting authority or in the permit.
13.0 Method Performance

13.1 Method detection limit (MDL)—MDLs from nine laboratories were pooled to develop the MDL of 0.5 μg/L given in Section 1.4 (Reference 15.12).

13.2 Data obtained from single laboratory testing of the method are summarized in Table 2 and show recoveries and reproducibility for “free” forms of cyanide, including the recovery and reproducibility of silver, nickel, and mercury cyanide species. Determination of these species tends to be problematic with other methods for the determination of available cyanide. As it is the case with other methods used for available cyanide, iron cyanide species were not recovered and recoveries for gold and cobalt species were zero or very low. The complete results from the single laboratory study are available in the Report of the Draft OIA Method 1677 Single Laboratory Validation Study (Reference 15.11).

13.3 Listed in Table 1 are the QC acceptance criteria developed from an interlaboratory validation study of this method. This study was conducted following procedures specified in the Guide to Method Flexibility and Approval of EPA Water Methods (Reference 15.10). In this study, a total of nine laboratories performed analyses for various water matrices. Table 3 shows a summary of the interlaboratory results which include the accuracy and precision data as % recoveries and relative standard deviations. In addition to spikes of easily dissociable cyanides, some samples contained known amounts of cyanides that are not recoverable (e.g., Pt and Fe complexes) and thiocyanate was spiked to one sample to investigate the potential for interference. The complete study results are available in the Report of the Draft OIA Method 1677 Interlaboratory Validation Study (Reference 15.12).

14.0 Pollution Prevention and Waste Management

14.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required. An overview of requirements can be found in Environmental Management Guide for Small Laboratories (EPA 233-B-98-001).

14.2 Samples containing cyanide, certain metals, and acids at a pH of less than 2 are hazardous and must be treated before being poured down a drain or must be handled as hazardous waste.

14.3 For further information on waste management, consult Less is Better: Laboratory Chemical Management for Waste Reduction, Reference 15.8.
15.0 References


15.5 ALPKEM CNSolution Model 3000 Manual. Available from ALPKEM / OI Analytical, Box 9010, College Station, TX 77842-9010.


15.8 Less is Better: Laboratory Chemical Management for Waste Reduction. Available from the American Chemical Society, Department of Government Regulations and Science Policy, 1155 16th Street, NW, Washington, DC 20036.

15.9 Handbook for Analytical Quality Control in Water and Wastewater Laboratories (EPA-600/4-79-019), USEPA, NERL, Cincinnati, Ohio 45268 (March 1979).


### 16.0 Tables

**Table 1. Quality Control Acceptance Criteria**

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Required Recovery Range (%)</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Precision and Recovery</td>
<td>92 - 122</td>
<td>&lt;5.1% RSD</td>
</tr>
<tr>
<td>Ongoing Precision and Recovery (Laboratory Control Sample)</td>
<td>82 - 132</td>
<td>N/A</td>
</tr>
<tr>
<td>Calibration Verification</td>
<td>86 - 118</td>
<td>N/A</td>
</tr>
<tr>
<td>Matrix Spike/Matrix Spike Duplicate</td>
<td>82 - 130</td>
<td>&lt;11% RPD</td>
</tr>
</tbody>
</table>

**Table 2. Species-Dependent Cyanide Recoveries Using Draft Method 1677\(^{(1)}\)**

<table>
<thead>
<tr>
<th>Species</th>
<th>0.20 µg/mL CN(^{-})</th>
<th>2.00 µg/mL CN(^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(CN)(_4)](^{2-})</td>
<td>97.4 (0.7)</td>
<td>98.5 (0.7)</td>
</tr>
<tr>
<td>[Cd(CN)(_4)](^{2-})</td>
<td>100.0 (0.8)</td>
<td>100.0 (0.2)</td>
</tr>
<tr>
<td>[Cu(CN)(_4)](^{2-})</td>
<td>100.9 (1.3)</td>
<td>99.0 (0.6)</td>
</tr>
<tr>
<td>[Ag(CN)(_4)](^{2-})</td>
<td>101.8 (0.9)</td>
<td>100.0 (0.5)</td>
</tr>
<tr>
<td>[Ni(CN)(_4)](^{2-})</td>
<td>104.3 (0.2)</td>
<td>103.0 (0.5)</td>
</tr>
<tr>
<td>[Hg(CN)(_4)](^{2-})</td>
<td>100.0 (0.6)</td>
<td>99.0 (0.3)</td>
</tr>
<tr>
<td>Hg(CN)(_2)</td>
<td>103.4 (0.4)</td>
<td>98.0 (0.3)</td>
</tr>
<tr>
<td>[Fe(CN)(_4)](^{2-})</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>[Fe(CN)(_6)](^{3-})</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>[Au(CN)(_2)](^{3-})</td>
<td>1.3(^(2)) (0.0)</td>
<td>0.0</td>
</tr>
<tr>
<td>[Co(CN)(_6)](^{3-})</td>
<td>2.9(^(2)) (0.0)</td>
<td>2.0(^(2)) (0.0)</td>
</tr>
</tbody>
</table>

1 Values are % recoveries; numbers in parentheses are percent relative standard deviations.
2 Commercial product contains some free cyanide.
Table 3. Cyanide Recoveries From Various Aqueous Matrices

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample CN Concentration</th>
<th>Added CN Concentration</th>
<th>Average % Recovery</th>
<th>% RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent water w/0.01M NaOH</td>
<td>0 µg/L</td>
<td>100 µg/L as KCN</td>
<td>108</td>
<td>4.0</td>
</tr>
<tr>
<td>POTW secondary effluent</td>
<td>3.0 µg/L</td>
<td>100 µg/L as KCN; 2 mg/L as [Pt(CN)]₄⁻</td>
<td>102</td>
<td>7.0</td>
</tr>
<tr>
<td>Petroleum Refinery Secondary Effluent</td>
<td>9.9 µg/L</td>
<td>2 mg/L as KCN; 5 mg/L as [Fe(CN)]₃⁻</td>
<td>87</td>
<td>21</td>
</tr>
<tr>
<td>Coke Plant Secondary Effluent</td>
<td>14.0 µg/L</td>
<td>50 µg/L as KCN</td>
<td>95</td>
<td>4.0</td>
</tr>
<tr>
<td>Rolling Mill Direct Filter Effluent</td>
<td>4.0 µg/L</td>
<td>none</td>
<td>80</td>
<td>41</td>
</tr>
<tr>
<td>Metals Finishing Indirect Primary Effluent</td>
<td>1.0 µg/L</td>
<td>200 µg/L as KCN; 2 mg/L as KSCN</td>
<td>92</td>
<td>16</td>
</tr>
<tr>
<td>Reagent water w/0.01M NaOH</td>
<td>0 µg/L</td>
<td>200 µg/L as KCN</td>
<td>101</td>
<td>8.0</td>
</tr>
<tr>
<td>Reagent water w/0.01M NaOH</td>
<td>0 µg/L</td>
<td>10 mg/L as KCN; 10 mg/L as [Pt(CN)]₄⁻</td>
<td>103</td>
<td>2.0</td>
</tr>
<tr>
<td>Mining Tailing Pond Effluent</td>
<td>842 µg/L</td>
<td>4 mg/L as KCN</td>
<td>98</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Cyano-complexes of Pt and Fe were added to the POTW and petroleum refinery effluents, respectively; and thiocyanate was added to the metals finishing effluent to demonstrate that the FI/LE system does not determine these forms of cyanide.

17.0 Glossary of Definitions and Purposes

The definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

17.1 Units of weights and measures and their abbreviations

17.1.1 Symbols

°C      degrees Celsius

%      percent

±      plus or minus

::  greater than or equal to

17.1.2 Alphabetical characters

 gram

 liter

 milligram

 milligram per liter

 microgram
17.2 Definitions

17.2.1 Available cyanide consists of cyanide ion (CN⁻), hydrogen cyanide in water (HCNₐ) and the cyano-complexes of zinc, copper, cadmium, mercury, nickel, and silver.

17.2.2 Calibration blank—A 100 mL volume of reagent water treated with the ligand-exchange reagents and analyzed using the FIA procedure.

17.2.3 Calibration standard (CAL)—A solution prepared from the dilution of stock standard solutions. A 100 mL aliquot of each of the CALs are subjected to the analysis procedure. The resulting observations are used to calibrate the instrument response with respect to the analyte concentration.

17.2.4 Discharge—Specific discharge (also known as "matrix type") means a sample medium with common characteristics across a given industrial category or industrial subcategory. Examples include: C-stage effluents from chlorine bleach mills in the Pulp, Paper, and Paperboard industrial category; effluent from the continuous casting subcategory of the Iron and Steel industrial category; publicly owned treatment work (POTW) sludge; and in-process streams in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory.

Specific discharge also means a discharge with characteristics different from other discharges. Therefore, if there are multiple discharges from a facility all with the same characteristics, these are the same discharge for the purpose of demonstrating equivalency of a method modification. In this context, "characteristics" means that results of the matrix spike and matrix spike duplicate (MS/MSD) tests with the unmodified method meet the QC acceptance criteria for recovery and relative percent difference (RPD).

17.2.5 Initial precision and recovery (IPR)—Four aliquots of the LRB spiked with the analytes of interest and used to establish the ability to generate acceptable precision and accuracy. An IPR is performed the first time this method is used and any time the method or instrumentation is modified.

17.2.6 Laboratory control sample (LCS)—An aliquot of LRB to which a quantity of mercury (II) cyanide stock solution is added in the laboratory. The LCS is analyzed like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.
17.2.7 Laboratory reagent blank (LRB)—An aliquot of reagent water that is treated like a sample including exposure to all glassware, equipment, and reagents that are used with other samples. The LRB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

17.2.8 Matrix spike/matrix spike duplicate (MS/MSD)—An aliquot of an environmental sample to which a quantity of the method analyte is added in the laboratory. MS/MSDs are analyzed like a sample. Their purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for the background concentration.

17.2.9 Minimum level (ML)—The level at which the entire analytical system shall give a recognizable signal and acceptable calibration point, taking into account method specific sample and injection volumes.

17.2.10 Ongoing precision and recovery (OPR)—See Laboratory control sample