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ANALYSIS OF CYANIDE IN MINING WATERS

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ABSTRACT

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Analysis of Cyanide in Mining Waters

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Cyanide, as a chemical compound, can be found in the effluents of numerous industries, particularly mining. The toxicity and concentration control of cyanide during gold and silver extractions necessitate the precise detection and determination of this compound. Therefore, this topic has been the focus of finding and then comparing experimentally the different available methods for analyzing cyanide.

In the theory part, numerous cyanide compounds in mining effluents were studied. Then, different analysis methods including titration, distillation, flow injection analysis, applying the alkaline solution of picric acid, ion selective electrode, and chromatographic methods were described. In the experimental part, silver nitrate titration as the most commonly applied methods in the gold extraction industry was selected to determine free cyanide concentrations in aqueous solutions.

In the experimental part, two series of experiments were conducted. In the first series, potassium iodide in the presence of ammonium hydroxide was used as an indicator. In the second sets of experiments, p-dimethylaminobenzylidene rhodanine was applied as the indicator. In both sets of the experiments, silver nitrate solution was utilized as the titrant for the determination of free cyanide concentration in the sodium cyanide solutions.

The results showed that the optimum sample volume for the analysis is 5 ml, and p-dimethylaminobenzylidene is the most reliable indicator. In addition, in the case of using this indicator, 0.00125 mol/liter silver nitrate is the most suitable concentration of the titrant for the analysis of cyanide in solutions containing 50-100 ppm free cyanide. Furthermore, 0.000125 mol/liter silver nitrate is the most suitable concentration of the titrant in solutions containing 1-10 ppm free cyanide.

Finally, the data were applied for the determination of free cyanide concentration in a synthetic mine water. According to the results, by using silver nitrate as the titrant and p-dimethylaminobenzylidene rhodanine as the indicator, it is feasible to determine the minimum concentration of 10 ppm free cyanide in the synthetic mine water. Also, the results showed that the presence of 1000 ppm sulfate, 10 ppm nitrate, 15 ppm ammonium, and 100 ppm chloride in the mine water did not cause significant interference.

LIST OF ABBREVIATIONS

$[Ag(CN)_2]^-$	Argentocyanide ion
$[Ag(NH_3)_2]^+$	Diamminesilver (I) ions
$Ag[Ag(CN)_2]$	Silver argentocyanide
Ag^+	Silver ion
Ag_2S	Silver sulfide
$AgCN$	Silver cyanide
AgI	Silver iodide
$AgNO_3$	Silver nitrate
ATP	Adenosine triphosphate
Au	Gold
$C_{12}H_{12}N_2OS_2$	P-dimethylaminobenzylidene rhodanine
C_2N_2	Cyanogen
$C_5FeN_6Na_2O$	Sodium nitroprusside
$C_6FeK_3N_6$	Potassium ferricyanide
$Ca(CN)_2$	Calcium cyanide
$Cd(CN)_2$	Cadmium cyanide
CH_3COCH_3	Acetone
Cl^-	Chloride
Cl_2	Chlorine
CN^-	Cyanide ion
$CNCl$	Cyanogen chloride
CNO^-	Cyanate
CO_3^{-2}	Carbonate
$Cu(CN)_2^-$	Dicyanide
$Cu(CN)_3^{-2}$	Tricyanide
$Cu(CN)_4^{-3}$	Tetracyanide
Cu_2S	Chalcocite
$CuCN$	Copper (I) cyanide
$CuFeS_2$	Chalcopyrite
DC	Direct current
DTPA	Diethylenetriamine penta-acetic acid

EC	Electrocoagulation
EDTA	Ethylenediaminetetraacetic acid
<i>FeS</i>	Pyrrhotite
FIA	Flow injection analysis
GC	Gas chromatography
<i>H₂O₂</i>	Hydrogen peroxide
<i>H₂SO₄</i>	Sulfuric acid
<i>H₃PO₄</i>	Phosphoric acid
<i>HCl</i>	Hydrochloric acid
<i>HCN</i>	Hydrogen cyanide
<i>Hg (CN)₂</i>	Mercury (II) cyanide
HPLC	High-Performance Liquid Chromatography
<i>HSO₃⁻</i>	Bisulfite
<i>I⁻</i>	Iodide
IC	Ion chromatography
ISE	Ion selective electrode
<i>KCN</i>	Potassium cyanide
<i>KI</i>	Potassium iodide
<i>MgCl₂</i>	Magnesium chloride
MP-P	Monopolar electrodes in parallel connection
MP-S	Monopolar electrodes in series connection
BP-S	Bipolar electrodes in parallel connection
<i>Na₂SO₄</i>	Sodium sulfate
<i>Na₄Fe (CN)₆·10H₂O</i>	Sodium ferrocyanide
<i>NaAu (CN)₂</i>	Sodium gold cyanide
<i>NaCl</i>	Sodium chloride
<i>NaCN</i>	Sodium cyanide
<i>NaNO₃</i>	Sodium nitrate
<i>NaOH</i>	Sodium hydroxide
<i>NH₂Cl</i>	Chloramine
<i>NH₃</i>	Ammonia
<i>NH₄⁺</i>	Ammonium
<i>NH₄Cl</i>	Ammonium chloride

NH_4OH	Ammonium hydroxide
$Ni (CN)_2$	Nickel (II) cyanide
NO_2^-	Nitrite
NO_3^-	Nitrate
OH^-	Hydroxide
$PbCO_3$	Lead carbonate
PbS	Lead (II) sulfide
S^{2-}	Sulfide
$S_2O_3^{2-}$	Thiosulfate
SAD	Strong acid dissociable
SCN^-	Thiocyanate
SO_3^{2-}	Sulfite
TDS	Total dissolved solids
WAD	Weak acid dissociable
$Zn (CN)_2$	Zinc cyanide

LIST OF SYMBOLS

I	electric current	, A
M	molarity	, $\frac{mol}{liter}$
M	mass	, kg
p	pressure	, Pa
t	time	, s
T	temperature	, k
V	electric potential	, V
V	volume	, m^3

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1 INTRODUCTION

Cyanide is a carbon/nitrogen compound that is present in different forms, such as free cyanide, simple cyanide compounds, metal-cyanide complexes, and cyanide-related compounds (Sentruk, 2013). This compound exists in gas, solid, and liquid form from numerous natural and anthropogenic sources; the natural source of cyanides is more than 2000 plant species (comprise cyanogenic glycoside), fungi, and microorganism such as bacteria (Simeonova & Fishbein, 2004.) Cyanide can be found in various effluents from several industries including coal coking, mining, ore leaching, metal electroplating, photography, and steel tempering (Moussavi, Majidi & Farzadkia, 2011).

Cyanide is widely used in various industry sectors including jewelry making, synthetic nylon, and rubber production, electroplating, agriculture, and mining (e.g. gold and silver extraction) (Kuyucak & Akcil, 2013). In the mining industry, gold and silver extractions are carried out via the cyanidation process. In this process, the high tendency of cyanide to complex with gold and silver results in the dissolution and removal of these precious metals from ore bodies; however, the affinity of cyanide to react with other metals in the ore results in its consumption (Norman & Raforth, 1994).

The released wastewater from the mining industry may contain metal-cyanide complexes. The change of pH or exposure to sunlight results in the ionization of these complexes and the release of free cyanide (Pohlandt, Jones & Lee, 1983). Free cyanide, as the sum up of molecular cyanide (HCN) and ionic cyanide (CN^-), is the primary toxic agent. According to the conducted research (EPA 2010a), 0.54 mg CN^- /kg weigh body is the oral lethal dose to humans.

To sum up, the toxicity of cyanide and the efficiency of the cyanidation process necessitate its rapid and precise determination. For this purpose, various techniques with their own advantages and disadvantages have been developed. These methods include titration, distillation, flow injection analysis, applying the alkaline solution of picric acid, ion selective electrodes, amperometric, and chromatographic methods. (Young et al, 2008, pp.731-735)

1.1 Objectives, research problems, and research questions

The main objective of this research was to compare different methods according to their accuracies, limitations, parameters, detection limits and define the best method for reliable analysis procedure. This study aims to answer four main question:

- Which indicator shows lower error in the determination of CN^- concentration via silver nitrate titration method?
- What is the optimum titrant concentration for the determination of specific CN^- concentration?
- Whether the presence of main interferences which may be found in mining water (sulfate, ammonium, chloride, and nitrate) affect the determination of CN^- concentration?
- What is the most suitable volume of the sample for the analysis of cyanide solutions?

1.2 Framework

The conceptual framework of this research is presented as a flowchart in figure 1.

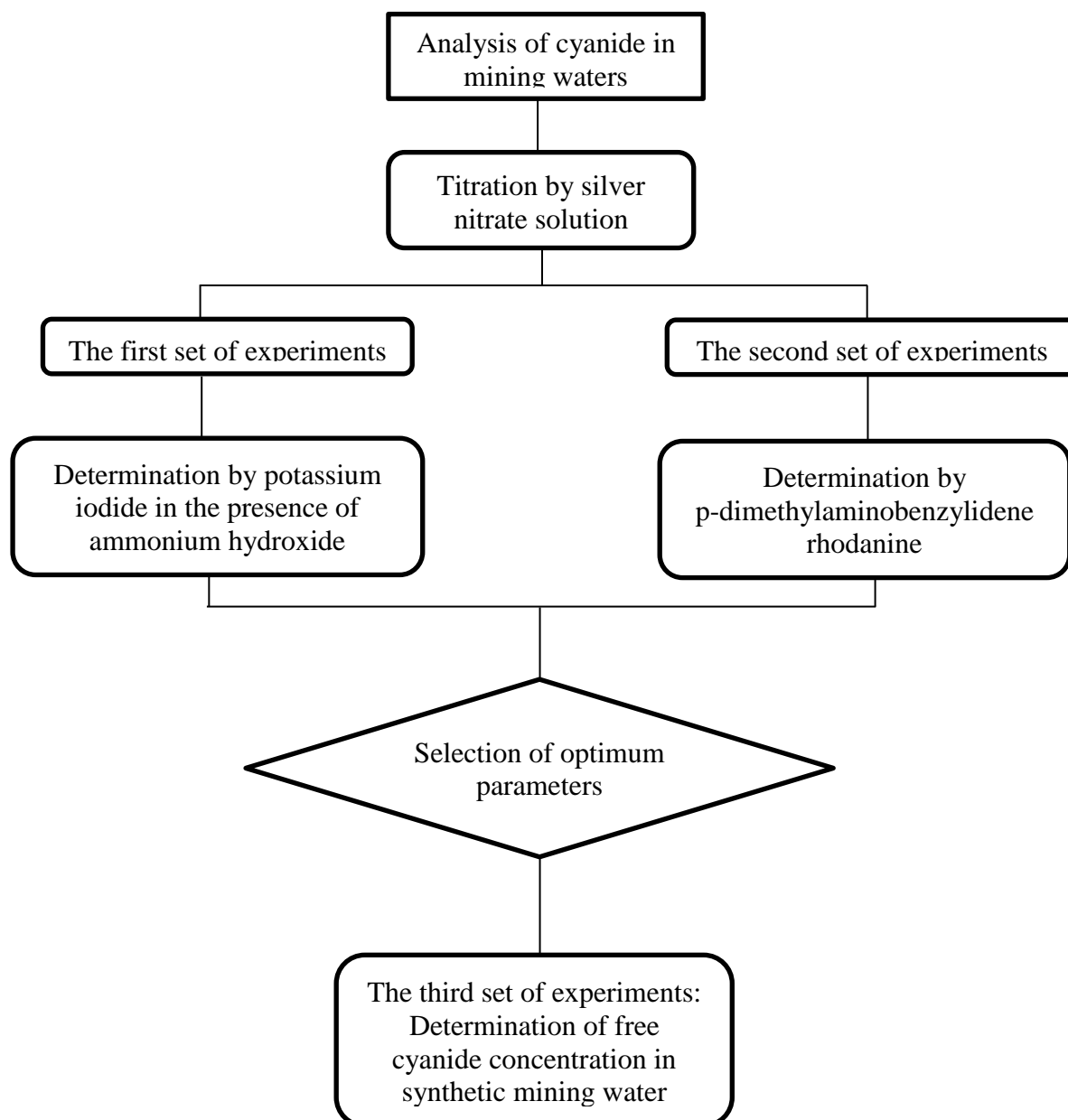


Figure 1. Framework and steps of the study.

LITERATURE REVIEW

Cyanide can be found in various environmental elements from a wide range of natural or anthropogenic sources. The toxicity and concentration control of cyanide in the mining industry (gold and silver extraction) make its precise detection necessary. Therefore, several methods have been developed to determine various types of cyanide. Different types of cyanide, its sources of occurrence, and the level of its toxicity to the environment, humans, and other living creatures are described in the following sections.

Cyanide complexes are classified into free cyanide, weak acid dissociable (WAD) cyanide, and total cyanide. The term free cyanide refers to either molecular hydrogen cyanide (HCN) or ionic cyanide (CN^-). The weak acid dissociable cyanide are cyanide species which dissociate in acidic condition (pH 4.5-6) and release free cyanide. Total cyanide or strong acid dissociable (SAD) cyanide refer to the all inorganic chemical forms of cyanide which release free cyanide in strongly acidic conditions.

Several methods including titration, distillation, flow injection analysis, applying the alkaline solution of picric acid, ion selective electrodes, amperometric, and chromatographic methods have been developed to determine different cyanide species. These methods, their drawbacks, advantages, procedure, and detection limit are also discussed in the next sections. Additionally, the removal of cyanide with natural degradation, chemical oxidation, and electrocoagulation are introduced at the end of this chapter.

2 CYANIDE

The term “cyanide” refers to the wide variety of chemical compounds, all of which contain CN moiety in their structure (Kuyucak & Akcil, 2013). Among all these chemical forms, free cyanide (sum of HCN and CN^-) is the primary toxic agent, regardless of its source (Simeonova & Fishbein, 2004). The chemical structure of CN^- in which one atom of carbon is bonded to one atom of nitrogen through a triple bond is shown in figure 2 (Birmingham City University, 2011).

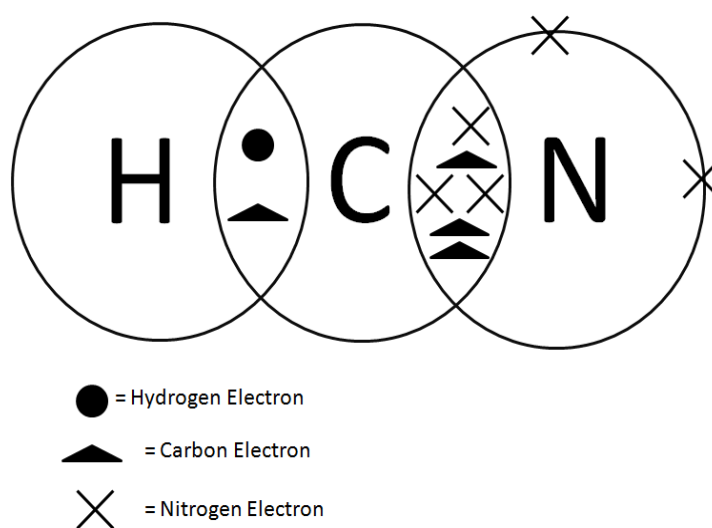


Figure 2. The chemical structure of cyanide ion (Birmingham City University, 2011).

The CN^- structure shows that nitrogen has three bonds and one unshared pair of the electron. Although, carbon has the same structure, its tendency to form four bonds makes CN^- unstable and highly reactive (Gary et al, 2014, p.169). The Lewis structure of CN^- in figure 3 represents one sigma (σ) bond, two pi (π), and two empty bonding orbitals. The s and p orbitals of this ion are filled with electrons and this makes cyanide behave similarly to a halogen (Pseudo-halogen behavior). The empty anti-bonding orbitals in this ion can form the bond with the d orbital of the transient metals which results in the formation of metal-cyanide compounds (Mudder, Botz & Smith, 2001, p.7).

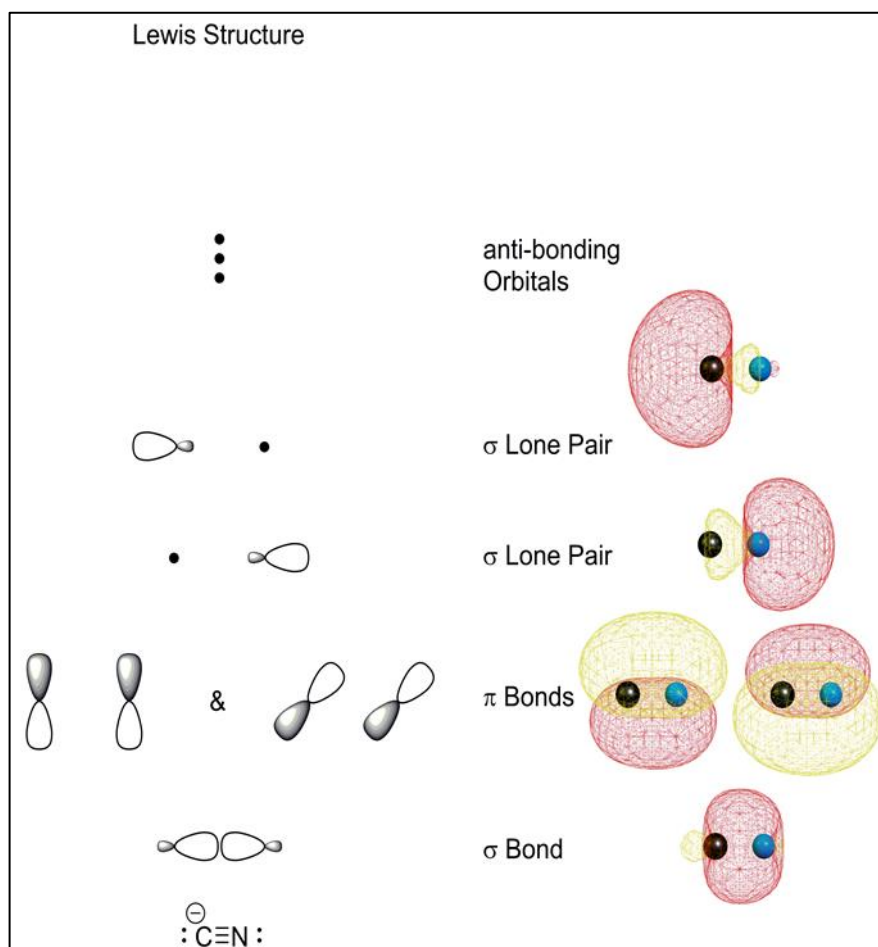


Figure 3. The Lewis structure of cyanide ion (Gary et al, 2014, p.169).

2.1 The occurrences of cyanide

Cyanide can be found naturally in the seeds/kernels, in the leaves, as well as in the roots of several plants. There are 2,650 plant species (that contain cyanogenic glycoside) in which the amount of cyanide in them can reach to more than 100 ppm. The cyanide concentrations in some plant species are summarized in table 1. (Lottermoser, 2010, pp.243-244)

Table 1. The cyanide concentrations in some plant species (Jaszczak et al, 2017; Logsdon, Hagestein& Mudder, 1999).

Plant species	Plant component(s)/types	Concentration
Bamboo	Tip	Max 8000 mg/kg
	Leaf	1010 ppm
	Stem	Max 3000 mg/kg
Cassava (sweet varieties)	Leaves	377-500 mg/kg
	Roots	138 mg/kg
	Dried roots	46-<100 mg/kg
	Mash	81 mg/kg
Cassava (bitter varieties)	Leaves	347-1000 mg/kg
	Roots	327-550 mg/kg
	Dried roots	95-2450 mg/kg
	Mash	162 mg/kg
Almond	Bitter	280-2500 mg/kg
	Sweet	22-54 mg/kg
	Spicy	86-98 mg/kg
Sorghum	Leaf	750 ppm
	Whole young plant	Max 2500 mg/kg
Apple	Seed	108 mg/100 gr
Plum	Seed	696 ppm
Manioc	Root	27 ppm
Spinach	Leaf	2.51±0.6 µg/g
Nectarine	Seed	196 ppm

Apart from natural occurrences of cyanide, there are anthropogenic sources which can introduce various forms of this compound to different environmental elements. Cyanide concentrations in the atmosphere, water, and soil from these sources are presented in table 2. (Simeonova & Fishbein, 2004)

Table 2. Cyanide concentrations in the atmosphere, water, and soil from anthropogenic sources (Eisler, 1991; Jaszczak et al, 2017; Kuyucak & Akcil, 2013).

Type of sample	Source of sample	Concentration
Atmosphere	Smoking tobacco	0.5 mg/cigarette
	Automobile exhaust: Adverse conditions Equipped with catalytic convertor	Max 10 mg/kg 1.1 mg/kg
	Gold field	0.76 ppb
	Fire	1.8±3 µg/m ³
Water	Electroplating waste:	
	Total cyanide	0.2; max. 3mg/kg
	Dissociable cyanide	0.07 mg/kg
	Complex cyanide	0.2 mg/kg
	Thiocyanate	0.02 mg/kg
	Road salt dock:	
	Total cyanide	25.6 mg/kg
	Dissociable cyanide	2.9 mg/kg
	Complex cyanide	23.1 mg/kg
	Thiocyanate	0
Soil	Gold cyanidation solution	540 mg/kg
	Oil refineries:	
	Total cyanide	0.01; max. 4mg/kg
	Dissociable cyanide	0
	Complex cyanide	0.0. Mg/kg
	Thiocyanate	2.2 mg/kg
	Coking plant sites (France)	46.5±14.5 mg/L
	Gold mine (Brazil)	0.83-1.44 mg/kg
	Techatticup (Mine sites in USA)	<0.01 mg/kg
	Coking plant sites (Germany)	0.14 mg/L

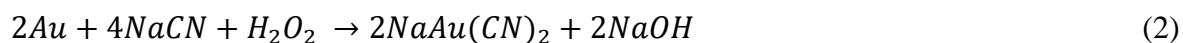
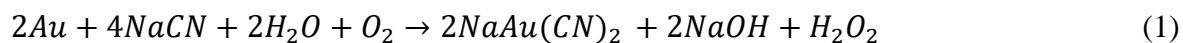
2.2 Applications of cyanide

Cyanide is a valuable chemical compound which is known as a major building block for the chemical industry. Therefore, annually more than 1.4 million tons of cyanide is produced and used in various industrial sectors. The applications of cyanide and cyanides compounds in some sectors are summarized in table 3. (Logsdon et al, 1999)

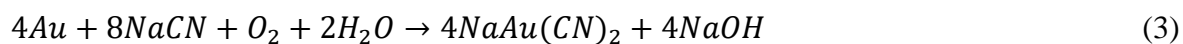
Table 3. The applications of cyanide and cyanide compounds in various sectors (Simeonova & Fishbein, 2004; Taylor, 2006).

Cyanide species	Chemical formula	Sector	Application
Calcium cyanide	$Ca (CN)_2$	–	As fumigant As stabilizer for cement
Cyanogen	C_2N_2	–	Fumigant Fuel gas for welding and cutting heat-resistant metals
Sodium nitroprusside Laetrile	$C_5FeN_6 Na_2O$ –	Pharmaceutic pharmaceutic	As anti-hypertensive agent Anticancer activity in animals
Sodium Ferrocyanide	$Na_4Fe (CN)_6.10H_2O$	photography	Bleaching
Potassium ferricyanide	$C_6FeK_3N_6$	Electroplating Calico printing	–
Sodium cyanide	$NaCN$	Mining Electroplating Transport	Extraction gold and silver – Fumigation of ships

The mining industry utilizes 13% of world cyanide production, mostly for gold extraction (Kuyucak & Akcil, 2013). The dissolution and removal of this precious metal can be carried out via several techniques; however, the cyanidation process is the most commonly applied method since 1898 (Mudder et al, 2001, p.1). The dissolution of gold is a two-step process in which hydrogen peroxide (H_2O_2) is produced as an intermediate (see reactions 1-3) (Norman & Raforth, 1994).



And the overall reaction is that is known as Elsner's reaction is:



The overall steps of gold processing are shown in figure 4. According to this figure, the gold ore is crushed to fine powder through the first step. After flotation, as the second step, if the gold ore is refractory (the microscopic particles of gold are mixed with silver, zinc, and copper) some pretreatment procedures such as roasting or oxidation should be applied prior to the leaching. This step is followed by cyanide leaching that can be either heap leaching (for low-grade ore) or agitate leaching (for high-grade ore). After that, the main objective is extracting the solubilized gold from the solution. The processing steps are described in more details in figure 5. (BarbenAnalytical, 2015; OCEANAGOLD, 2015)

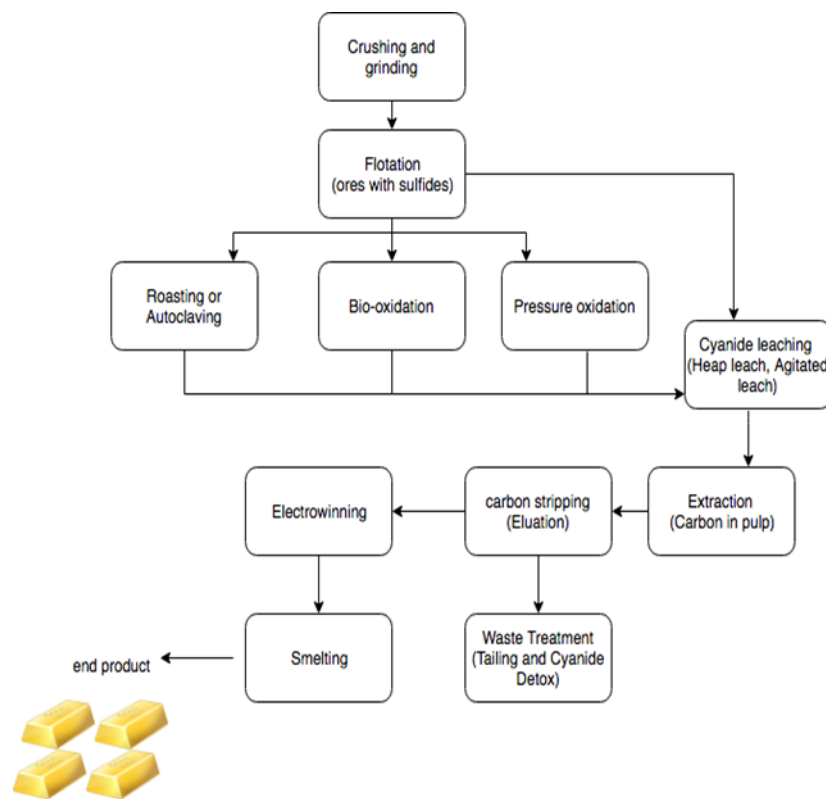


Figure 4. The block diagram of gold processing (BarbenAnalytical, 2015).

According to figure 4 to figure 5, the extracted pulp from the leaching step is cascaded over 4-6 tanks via gravity flow. Next, the added activated carbon at the contrary end is pumped upstream through the tanks. The final loaded carbon is separated and transferred to the carbon stripping step. In this stage, the movement of the loaded carbon through the stripping vessel (at high pH and temperature around 95°C) results in the gold desorption from the carbon. The resultant solution which contains the gold is known as the pregnant leach solution. (BarbenAnalytical, 2015; OCEANAGOLD, 2015)

The pregnant solution is transferred to the electrowinning cell through the next stage. At the same time, the regenerated carbon is also carried away to the carbon adsorption cell. The applied current into the solution in the electrowinning cell breaks the bond between cyanide and gold. At the end of the process, the accumulated gold on the electrowinning cathodes is melted in the smelting stage for further processing and the barren cyanide solution is conveyed to the leaching circuit. (BarbenAnalytical, 2015; OCEANAGOLD, 2015)

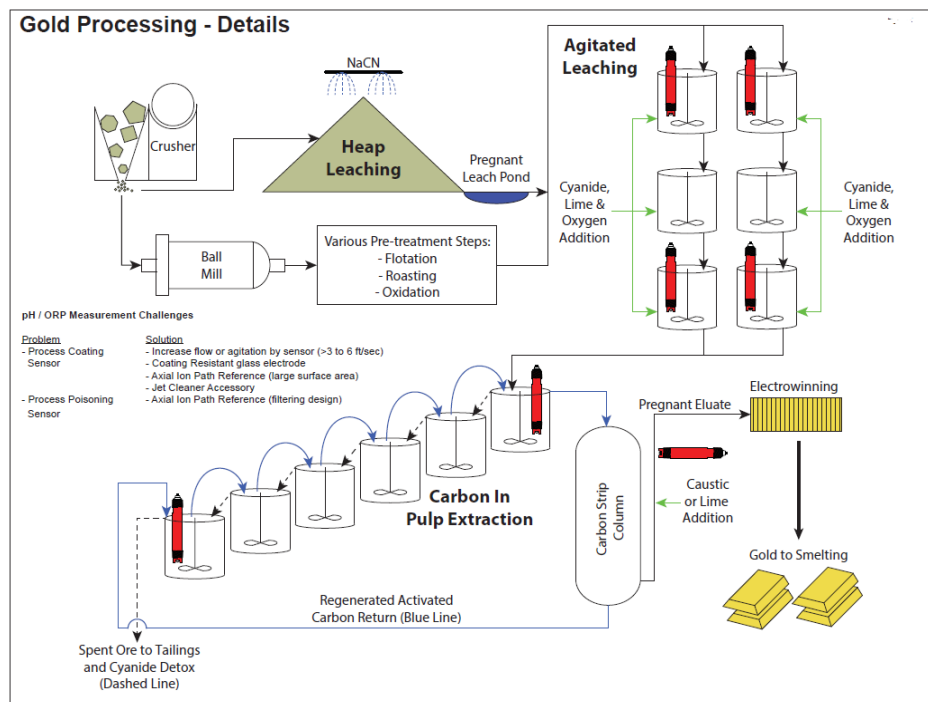


Figure 5. The details of gold processing steps from figure 4 (BarbenAnalytical, 2015).

2.3 The chemistry of cyanide solutions

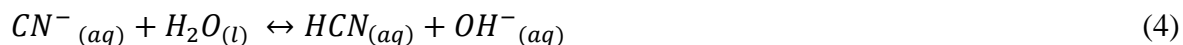
The cyanide compounds present in gold mine, cyanidation solutions, or discharged effluents include free cyanide, simple cyanide compounds, metal-cyanide complexes, and cyanide-related compounds. The classification of these compounds is presented in table 4 and the grouping of each one is described in the following subsections. (Mudder et al, 2001, p.6)

Table 4. Classification of cyanide and cyanide compounds in cyanidation solutions (Mudder et al, 2001, p.9).

Classification	Examples of cyanide compounds
Free cyanide	HCN , CN^-
Simple cyanide compounds	Soluble: $NaCN$, KCN , $Ca(CN)_2$, $Hg(CN)_2$ Insoluble: $Zn(CN)_2$, $Cd(CN)_2$, $CuCN$, $Ni(CN)_2$, $AgCN$
Metal-cyanide complexes	Weak complexes: $Zn(CN)_4^{2-}$, $Cd(CN)_3^{2-}$, $Cd(CN)_4^{2-}$ Moderately strong complexes: $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Ni(CN)_2^{2-}$, $Ag(CN)_2^-$ Strong complexes: $Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Au(CN)_2^-$
Cyanide-related compounds	SCN^- , CNO^- , NO_3^- , NH_3 , $CNCl$, NH_2Cl

2.3.1 Free cyanide

The term free cyanide refers to the sum of CN^- and HCN . The dissolution of $NaCN$ in the cyanidation process results in the formation of Na^+ and CN^- . Cyanide anions undergo hydrolysis and combine with hydrogen according to reaction 4. (Lottermoser, 2010, p.246)



Parameters such as pH, the salinity of solution, and the content of heavy metals which tend to react with cyanide determine the concentration of free cyanide in the solution (Pohlandt, Jones & Lee, 1983). The presence of CN^- and HCN as the function of pH is presented in figure 6. According to this figure, under alkaline conditions ($pH > 10.5$), the dominant species are CN^- . At the lower pH values (around 9.3), there is the equivalent concentration of CN^- and HCN (Lottermoser, 2010, p.246). In addition, free cyanide is present as HCN from the neutral to acidic conditions ($7.0 < pH < 8.3$).

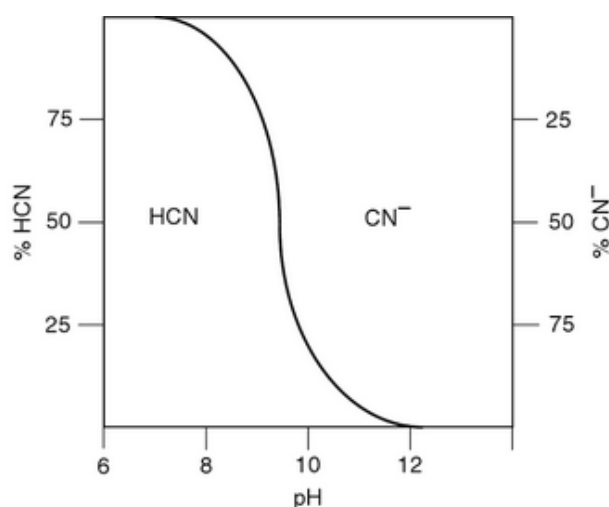


Figure 6. The presence of free cyanide species as the function of pH at 25 °C (Lottermoser, 2010, p.246).

Hydrogen cyanide is a weak acid with bitter almond-like odor, low boiling point (25.70 °C) and high vapor pressure (35.2 kPa at 0 °C, 107.2 kPa at 27.2 °C), which readily is converted to gas and dispersed into the air (Mudder et al, 2001, p.7; Simeonova & Fishbein, 2004). The formation of *HCN* is the minor factor in reducing the cyanide concentration in mineral processing solutions; however, the main reason for the cyanide consumption at mining sites can be because of its high tendency to complex with other metals in ore bodies (Moran, 1999).

2.3.2 Simple cyanide compounds

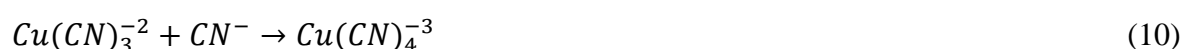
The simple cyanide compounds are divided into readily soluble neutral and insoluble salts. The soluble simple cyanide compounds are alkali and alkali earth metal cyanides such as calcium, potassium, and sodium. These compounds are dissolved readily in aqueous solution and produce CN^- and metal cations according to reactions 5-7. This is followed by reaction of CN^- with water and the formation of *HCN* as it is shown in reaction 4. (Barnes et al, 2000; Mudder et al, 2001, p.8)





2.3.3 Metal-cyanide complexes

The metal-cyanide complexes are divided into weak, moderately strong, and strong complexes. The tendency of cyanide to complex with metals such as copper, nickel, zinc, silver, and cadmium results in the formation of weak and moderately strong complexes. These complexes are formed in a step-wise way in which the cyanide content is increased as the cyanide concentration in the solution gets higher. For example, the formation of copper-cyanide complex takes place according to reaction 8-10. (Mudder et al, 2001, pp.12-13)



The ability of cyanide to complex with copper, iron, and gold results in the formation of strong metal-cyanide complexes. These compounds are stable in acidic solutions at room temperature, however, they decompose to some extent at elevated temperature (Barnes et al, 2000). The dissociation of these compounds due to the exposure to UV radiation or highly strong acid can release considerable amounts of CN^- . The iron-cyanide complexes are known for releasing HCN through exposure to intense UV radiation (Mudder et al, 2001, p.13). The dissociation rate of metal-cyanide complexes is affected by several parameters such as the water temperature, pH, total dissolved solids, complex concentration, and light intensity (Moran, 1999).

2.3.4 Cyanide related compounds

The cyanide-related compounds include thiocyanate, cyanate, cyanogen chloride, chloramine, ammonia, and nitrate which are formed in the solution as the result of cyanidation, water treatment processes, or natural attenuation (Mudder et al, 2001, p.22). Thiocyanate (SCN^-) is generated in the reaction between CN^- and sulphur species during the

leaching or pre-aeration processes. The potential sources of sulphur include free sulphur, all the sulphide minerals such as pyrrhotite (FeS) chalcocite (Cu_2S) and chalcopyrite ($CuFeS_2$) and the oxidation products of them, such as polysulfide and thiosulfate ($S_2O_3^{2-}$) (Kuyucak & Akcil, 2013). Some of the reactions which result in the formation of thiocyanate are presented in table 5.

Table 5. Chemical reactions which result in thiocyanate generation (Jenny et al, 2001).

Reaction agent	Reaction
Elemental sulfur	$S^0 + CN^- \rightarrow SCN^-$
Sulfide	$S^{2-} + CN^- + H_2O + 1/2O_2 \rightarrow SCN^- + 2OH^-$
Thiosulfate	$S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^-$

Thiocyanate is seven times less toxic than cyanide and has inferior tendency to form soluble metal complexes. However, its biological and chemical degradation may produce ammonia, cyanate, and nitrate. (Kuyucak & Akcil, 2013; Mudder et al, 2001, p.22)

Cyanate (CNO^-) is another cyanide-related compound which can be generated via the oxidation of cyanide with the aid of oxidizing agents such as hydrogen peroxide, ozone, gaseous oxygen or hypochlorite. The hydrolysis of this compound to ammonia and carbonate (CO_3^{2-}) inhibits its accumulation in the solution. Some of the reactions which result in the cyanate formation are listed in table 6. (Kuyucak & Akcil, 2013; Simovic, 1984)

Table 6. Chemical reactions that result in cyanate generation.

Reaction agent	Reaction	Reference
Hydrogen peroxide	$CN^- + H_2O_2 \rightarrow CNO^- + H_2O$	(Kitis et al, 2005)
Ozone	$CN^- + O_3 \rightarrow CNO^- + O_2$	(Parga et al, 2003)
Hypochlorite	$CN^- + ClO^- \rightarrow CNO^- + Cl^-$	(Lister, 1955)

The other compound belonging to this group is cyanogen chloride ($CNCl$) which is produced due to the destruction of cyanide by ClO^- in alkaline chlorination process. This toxic compound is not stable and is converted to CNO^- in few minutes at pH values from 10 to 11. There is indeterminacy about the behavior of $CNCl$ at lower pH levels. (Eden, Hampson & Wheatland, 1950)

Two other cyanide-related compounds are Chloramine (NH_2Cl) and ammonia (NH_3). Chloramine is chlorinated ammonia compound that can be generated during alkaline chlorination process. This compound is less toxic than CN^- ; however, it may persist in the environment for a substantial period (Moran, 1999). The presence of ammonia in mining sites can be from remaining blasting agents, hydrolysis of cyanate, or the oxidation of hot cyanide solution during stripping of loaded carbon. Free ammonia tends to form soluble amine complexes with heavy metals such as zinc, silver, copper, and nickel. Hence, the presence of ammonia in the solutions with the pH values above 9 prevent the precipitation of these metals (Mudder et al, 2001, p.23).

Finally, Nitrate (NO_3^-) and Cyanogen (C_2N_2) can also be considered as cyanide-related compounds. The oxidation of ammonia through the biological nitrification results in the formation of nitrite and then nitrate, which is a relatively stable compound. High concentrations of nitrate (more than 45 mg/liter) can be detrimental to humans, especially infants. Moreover, this biological nutrient can accelerate the growth of algae in the water. The consumption of dissolved oxygen by these species can endanger the life of aquatic organisms, particularly fish (Botz, Mudder & Akcil, 2005, pp.693-697). The free cyanide can also form C_2N_2 under acidic conditions and in the presence of oxidants such as oxidized copper minerals. Cyanogen exists in a gaseous form at ambient temperature, however, the stability of this compound at moderately alkaline or neutral pH waters is unclear (Moran, 1999).

2.4 Toxicity of cyanide

Cyanide is a fast-acting poison, which can enter the body as hydrogen cyanide via the lungs, skin absorption, and from the mucous membrane. This compound can also be absorbed as an ion through ingestion. (Egekeze & Oehme, 2011) The combination of cyanide as HCN with Fe^{+3} of the cytochrome oxidase results in cellular hypoxia and shifting from aerobic to anaerobic cellular respiration (Surleva, Gradinaru & Drochioiu, 2012). This alteration leads to cellular ATP reduction, tissue death, and an increase in the synthesis of lactic acid, as shown in figure 7.

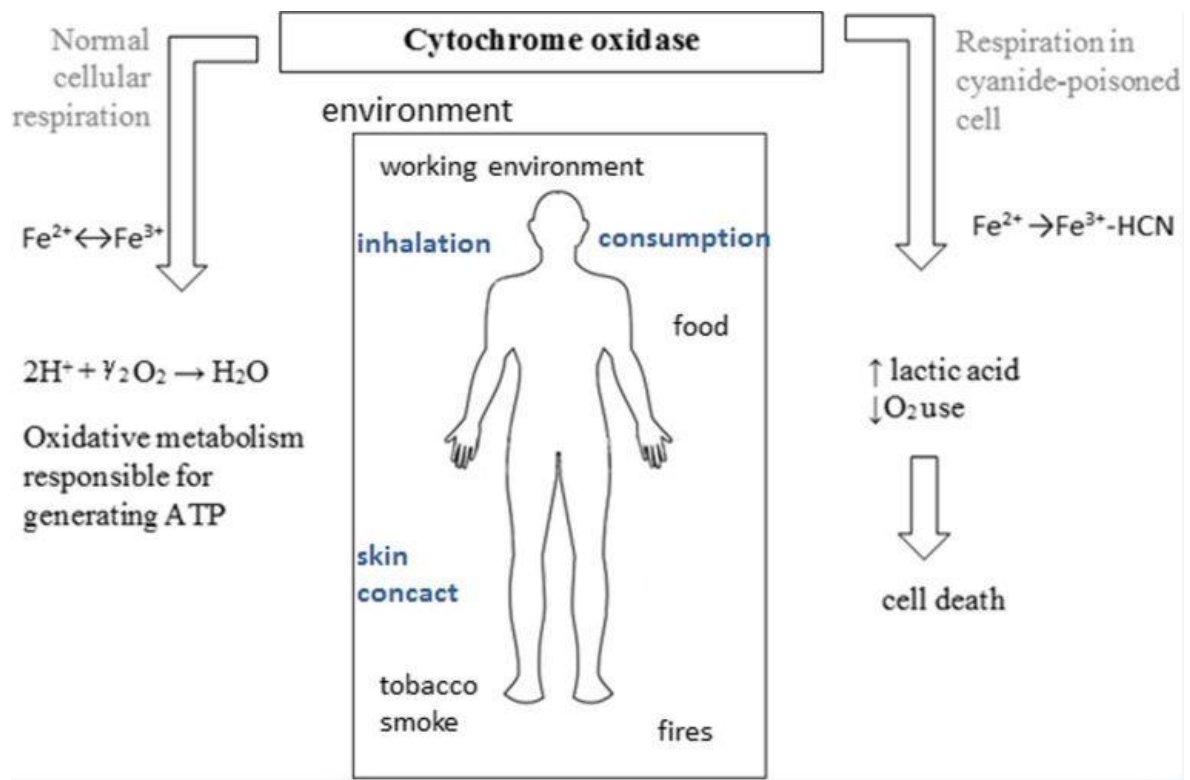


Figure 7. The impact of cyanide on the human body (Jaszczak et al, 2017).

There are various sources of exposure to cyanide and cyanide compounds; however, these components do not accumulate in tissues since the body converts them to thiocyanate. This compound, which is seven times less toxic than cyanide, is excreted in the urine after the transformation (Logsdon et al, 1999, p.27). Cyanide is not carcinogenic; however, the chronic exposure to cyanide can cause weakness, damage to kidney, miscarriage, and hypothyroidism. The toxicity of cyanide depends on the type of compound, which contains cyanide ion, as well as the source of its occurrences (Jaszczak et al, 2017). The effects of cyanide on some living creatures are summarized in table 7.

Table 7. The effect of cyanide on some living creatures (Donato et al, 2007; Jaszczak et al, 2017; Mudder et al, 2001, p.147; Singh & Wasi, 1986).

Species	Dose	Comment
Rat	5.1-5.7 mg <i>NaCN</i> /kg BW	*LD50 lethal single dose
Dog	24 mg <i>NaCN</i> /kg BW	Lethal single dose
Domestic chicken	11.1 mg <i>CN</i> /kg BW	Acute oral LD50
Gold fish	104 mg nickel cyanide compound/liter	No effect in 24 hr
Rainbow Trout	0.028 mg <i>HCN</i> /liter	**LC50-96 hr
Rainbow Trout	0.01 mg <i>KCN</i> /liter (T=2-4°C)	LC50-96hr
Adult human	0.57 mg <i>HCN</i> /kg BW 1.5mg <i>CN</i> /kg BW 200-300 mg cyanide in food	Death Lethal dose Lethal dose
Guinea pig	1.098 mg/kg ammonia, thiosulphate	LD50
Rabbit	2.680 mg/kg sodium nitrate	LD50
<p>*LD50 is a lethal dose, usually given in mg/kg-body weight. The dose means the organism ingests the toxic substance.</p> <p>**LC50 is a lethal concentration to which and organism is exposed. For example, fish or daphnia are placed in water with a concentration of the toxic substance.</p>		

3 THE CYANIDE ANALYSIS METHODS

The precise determination of cyanide is difficult for several reasons. As an example, the presence of cyanide in the ionic or molecular form is highly dependent on the pH of the solution. Furthermore, the high tendency of cyanide to complex with different metals results in the formation of metal-cyanide complexes. Additionally, the ionization of these complexes through exposure to sunlight or change of pH releases substantial concentrations of *HCN*. (Barnes et al, 2000)

The chemical solution which contains *HCN* and the precipitate of cyanide complexes is not stable, and its analysis is difficult. Accordingly, various methods with their own advantages and disadvantages have been developed for the determination of cyanide. The most frequently used methods in laboratories for cyanide analysis are discussed in the following chapters. (Pohlandt et al, 1983)

3.1 Titration

Titration is the most commonly applied method for the determination of free cyanide concentration in gold extraction industry (Young et al, 2008, p.731). This technique is based on the addition of titrant with a known concentration to a specific volume of a sample with unknown concentration (Harvey, 2000, p.274). The change of color or the potential of the electrode shows the completion of titration and is known as the end-point. These changes, which can be detected either visually or instrumentally, are described in the followings (Bark & Higson, 1963). A typical setup of titration is shown in figure 8.

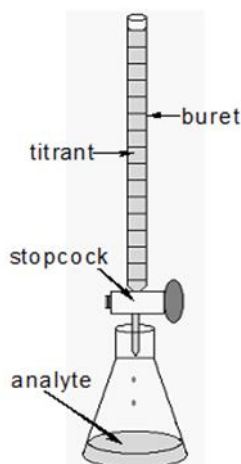


Figure 8. A titration setup for typical laboratory applications (Chemistry102, 2013).

3.1.1 Titration method including visual end-point determination

The first visual determination method of cyanide was reported by Liebig in 1851. In this method, the sample containing cyanide is titrated with silver nitrate solution, $AgNO_3$. The reaction between silver ions and CN^- according to reaction 11 results in the formation of argentocyanide ion, $[Ag(CN)_2]^-$. When the reaction is completed, further addition of titrant yields the insoluble silver argentocyanide ($Ag[Ag(CN)_2]$) as it is shown in reaction 12. Finally, the endpoint is detected by the formation of perpetual turbidity or the precipitate. (Singh & Wasi, 1986)

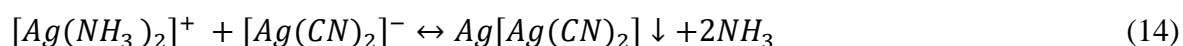


The Liebig's argentometric method is subjected to the error in ammoniacal and alkaline solutions (Bark & Higson, 1963). In 1895, Denigés modified this method by adding potassium iodide (KI) as the indicator in the presence of ammonium hydroxide (NH_4OH) prior to the titration (Singh & Wasi, 1986). In the modified method, the formation of silver iodide (AgI) which appears as an insoluble yellowish solid, shows the completion of the titration (Milosavljevic, 2013).

In the Denigés method, the added silver ions to the solution are converted to diamminesilver (*I*) ions, $[Ag(NH_3)_2]^+$. This is followed by the reaction of these ions with two CN^- and the formation of $[Ag(CN)_2]^-$ according to reaction 13. (Burgot, 2012, pp.700-701)



The excess amount of silver ion as $[Ag(NH_3)_2]^+$ will react with $[Ag(CN)_2]^-$ according to the following reaction (Burgot, 2012, pp.700-701).



Finally, the added iodide (*I*) in the form of *KI* causes the precipitation of silver iodide as it is shown in reaction 15 (Burgot, 2012, pp.700-701).



In 1944, Ryan and Culshaw modified the Liebig's method by using p-dimethylaminobenzylidene rhodanine ($C_{12}H_{12}N_2OS_2$) indicator. In this method, once all CN^- reacted with Ag^+ according to reaction 11, the excess amount of silver ions reacts with the rhodanine accordingly, and the color change from yellow to pale pink occurs (see reaction 16). In other words, the end-point of the process is reached when the pale pink color appears. (Breuer, Sutcliffe & Meakin, 2011) This method can be successfully used for the determination of cyanide concentration in samples with 1 ppm and higher free cyanide (Bark & Higson, 1963).



Other applied indicators in the determination of cyanide with $AgNO_3$ includes dithizone and diphenylcarbazide. In the case of using dithizone, the end-point is detected by the change of color from orange-yellow to deep red-purple. Regarding diphenylcarbazide, the addition of titrant is stopped when the color changes from pink to pale violet. (Archer, 1958; Mendham 2006, p.358)

Sarwar et al. (1973) studied the feasibility of using other solutions than AgNO_3 for the determination of cyanide concentration. They reported that N-bromo-succinimide as titrant and bodeaux red as an indicator can be applied for the detection of 1-6 mg/ml of cyanide with the standard deviation of 0.66%. In their experiment, the change of color from rose-red to yellow showed the end of the titration. However, the presence of iodide, thiocyanate, bisulfite (HSO_3^-), thiosulfate, sulfite (SO_3^{2-}) and sulfide (S^{2-}) interfered with the precise determination of cyanide. (Sarwar, Rashid & Fatima, 1973)

3.1.2 Titration method including instrumental end-point determination

The first instrumental determination method of cyanide using AgNO_3 with potentiometric electrode was introduced in 1922 (Bark & Higson, 1963). In this method, the potential change of the electrode (mostly silver) is measured against the reference electrode during the addition of titrant (Jimenez-Velasco et al, 2014). In the potential curve, which is obtained by plotting the electrode potential changes versus the added volume of titrant, the sharp peak shows the end-point and can be related to the concentration of free cyanide, as it is shown in figure 9.

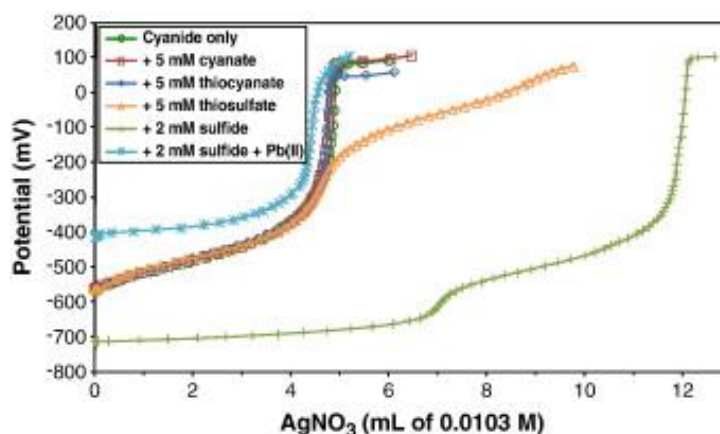


Figure 9. The potential change curve in the presence of various anions (Breuer et al, 2011).

Breuer et al. (2011) compared the determination of cyanide using silver nitrate titration with rhodanine and silver nitrate titration using the potentiometric end-point method. They reported that in the presence of copper and/or thiosulfate, the first method presents overestimated concentration for free cyanide. However, in the potentiometric end-point, if the pH is above 12 (to eliminate the interference of zinc), this method has no interference. Although the analysis using rhodanine could not be compared directly in contrast to the

potentiometric end-point, the potentiometric method was selected as a preferable technique (Breuer et al, 2011). Jimenez-Velasco et al. (2014) studied the analysis of cyanide in copper-bearing solution with different endpoint detection methods. The rhodanine, *KI* indicator, and potentiometric method were applied for the determination of free cyanide concentration. The above-mentioned methods showed the overestimation of about 25.2%, 4.5%, and 0.3% in samples with low copper content (molar ratio $CN/Cu \approx 8$). This overestimation in samples with high copper content (molar ratio $CN/Cu \approx 4$) was 121%, 56%, and 8%, respectively (Jimenez-Velasco et al, 2014). The other interference that can be found in the cyanide solution is S^{2-} . In the titration procedure, the added silver ions react with sulfide and form the black solid of silver sulfide (Ag_2S) which hamper the visual detection of end-point. Alonso-González et al. (2017) studied the determination of free cyanide in the presence of sulfide ion with potentiometric end-point detection method. They reported that this method can be successfully applied for the measurement of free cyanide and sulfide ion concentrations separately (Alonso-González et al, 2017).

According to the literature, silver nitrate titration is a reliable method for the determination of free cyanide concentration. In addition, this technique can determine the concentration of WAD or total cyanides after distillation procedure which is described in the following section. In order to avoid the volatilization of hydrogen cyanide, the pH of the solution is maintained at 12 by addition of sodium hydroxide ($NaOH$) before the commencement of titration. The titration of the cyanide solution containing complexing metals quantify all free cyanides, cyanides associated with zinc, and the portion of those associated with copper. In this case, the obtained results are titrable cyanide rather than free cyanide. However, this method does not act precisely when the concentration of copper is high ($CN/Cu \approx 4$). In this case not only the obtained data for the free cyanide is not precise enough, but also all the associated cyanides with the copper are not quantified. (Milosavljevic, 2013; Young et al, 2008, p.732)

In conclusion, the titration method is prone to error in the cyanide solution containing copper, thiosulfate, and sulfide. In the presence of two latter interferences, by applying the potentiometric end-point detection method, the concentration of cyanide and thiosulfate (Young et al, 2008, p.732), cyanide and sulfide (Alonso-González et al, 2017) can be measured individually. However, in the presence of copper, due to the emerging of several

end-points, the determination is problematic. Breuer and Rumball in 2006 determined free cyanide and tetracyanide ($Cu(CN)_4^{3-}$) concentration via modifying the determination of end-point. However, it is worth to mention that this study was performed on the synthetic water and in the analysis of process solution, the small peaks on the curve may be masked via other titrable species of $AgNO_3$ (Young et al, 2008, p.732).

3.2 Distillation

Distillation can be applied as a pretreatment method for the determination of WAD and total cyanide (Nollet & De Gelder 2007, p.367). In this technique, the sample is acidified and boiled until the cyanide is liberated from various cyanide compounds in the solution. The released cyanides as HCN gas are trapped in the absorption solution. Finally, the cyanide concentration is determined via an appropriate procedure (Young et al, 2008, p.732).

The determination of WAD cyanide by distillation procedure can be found in test method C from ASTM D2036-06 and standard methods 4500-CN I from APHA, 4500-NO3. For the analysis, the sample is placed in the distilling flask and buffered at pH 4.5-6 by adding zinc acetate and acetate buffer; After that, 2 to 3 drops of methyl red indicator are added to the sample (the obtained solution should be pink). This procedure is followed by heating the sample until its boiling point followed by one hour of reflux distillation. The final product of the procedure is a liberated cyanide. (APHA 4500-NO3; ASTM D2036-06)

The liberated HCN is trapped in the absorption solution ($NaOH$). After this, the concentration of cyanide in this solution is determined with titrimetric, colorimetric, or ion selective electrodes (ASTM D2036-06; APHA 4500-NO3). By means of this method, all the free cyanide and the cyanide ions associated with cadmium, copper, zinc, and nickel are recovered and quantified (Mudder et al, 2001, p.40). The cyanide distillation apparatus is shown in figure 10.

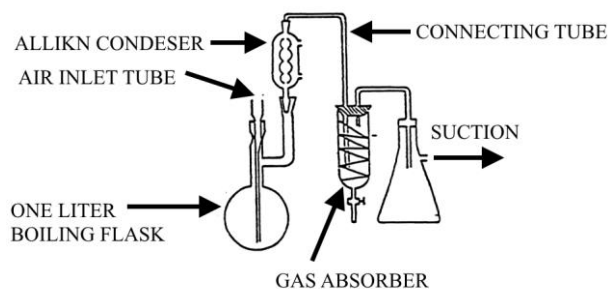


Figure 10. Cyanide distillation apparatus (ASTM D2036-06).

In addition to the measurement of WAD cyanide, this procedure can be also used for the total cyanide determination. In this method, magnesium chloride ($MgCl_2$) is added as a catalyst into the sample through the air inlet tube. To adjust the pH of the sample to values less than 2, sulfuric acid (H_2SO_4) is introduced through the same tube. This pH facilitates the dissociation of iron-cyanide complexes at high temperature. After boiling and one hour of reflux distillation, the concentration of cyanide in the absorption solution is determined by colorimetric, titrimetric, ion selective electrode, or flow injection ligand exchange with amperometric detection methods. (APHA 4500-NO₃; ASTM D2036-06)

To sum up, distillation can be used as the pretreatment method for the determination of WAD and total cyanide concentrations. However, the required amount of sample for each test is around 500 ml and the analysis time is long (1-2 hours). Moreover, the presence of nitrate, nitrite, thiocyanate, and sulfide can interfere with the precise determination; however, the determination of WAD cyanide is less susceptible to the presence of thiocyanate and sulfide. The effects of these interferences and the elimination procedure of them are summarized in table 8. (APHA 4500-NO₃; ASTM D2036-06)

Table 8. The effects interferences on cyanide distillation method and their elimination procedures (APHA 4500-NO₃; ASTM D2036-06; Barnes et al, 2000; Mudder et al, 2001, p.34; Young et al, 2008, pp.732-733).

Interferences	Effect of interferences	Elimination of interferences
Nitrate and nitrite	Formation of transient compounds which decompose in test condition and generate CN^- (Overestimated results are obtained).	Addition of sulfamic acid before the addition of sulfuric acid.
Sulfide	It is distilled over with cyanide and produce hydrogen sulfide during distillation.	Addition of lead carbonate ($PbCO_3$) to the solution prior to distillation.
Thiocyanate	In the acidic condition, it reacts with nitrate and generates free cyanide (overestimated results are obtained). In the colorimetric procedure, it reacts with chloramine-T and both ions are colorized.	Using H_3PO_4 instead of H_2SO_4 .

3.3 Flow Injection Analysis (FIA)

Flow Injection Analysis is an automatic or semi-automatic analytical technique that emerged in 1975 (Ghous, 1999). In this method, a specific volume of the sample is injected into the carrier stream, which flows continuously. The injected sample constitute a zone, which then is carried toward a detector that constantly records changes of absorbance by monitoring the potential of an electrode. In addition to the electrode potential, any other physical parameter resulting from the passing of the sample through the flow cell can be used for the determination (Hansen & Wang, 2004). Schematic of the FIA system and its stages are depicted in figure 11. Finally, it is worth to mention that the FIA method has its own drawbacks. As an example, the presence of sulfide can interfere with the analysis of cyanide in this method. However, this interference can be eliminated by adding lead salt before injecting the sample to the analyzer (Sulistiyarti et al, 1999).

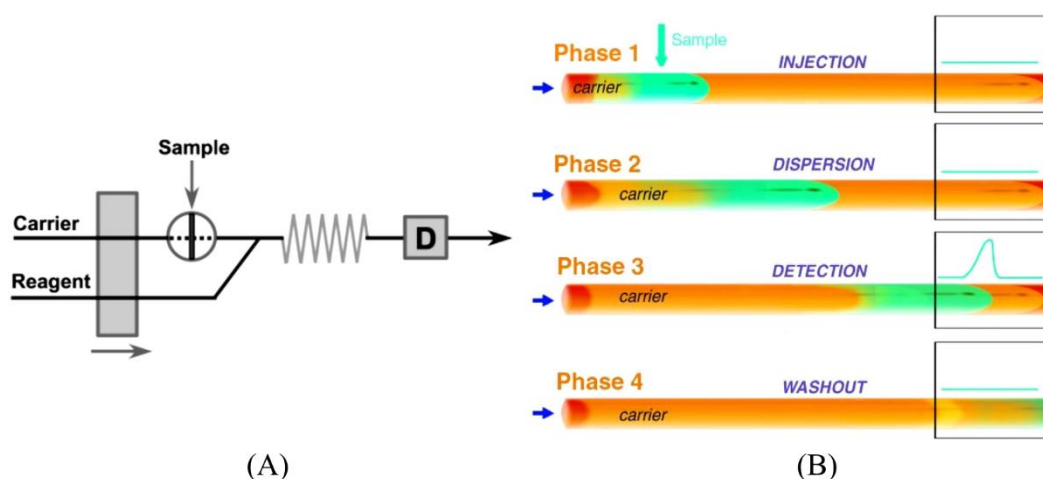


Figure 11. A) Typical representation of FIA system; B) Stages of FIA (Hansen & Wang, 2004; Siddiqui, Alothman & Rahman, 2017).

Dai (2005) investigated the determination of free cyanide, dicyanide ($Cu(CN)_2^-$), and tricyanide ($Cu(CN)_3^{2-}$) in gold leaching solutions via developed FIA method. The system used in the study employed a flow-through electrochemical cell. This cell comprised of a platinum electrode, a silver electrode, and a membrane, which provided the flow channel for the sample over the electrode's surfaces. They applied the potential of -150 mV and measured the charge during the silver oxidation. According to their results, the measured charge was linearly relevant to the free cyanide concentration. The oxidation of silver at 100 mV and reduction of copper at -650 mV were used for the determination of $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$ species respectively. (Dai, 2005)

This method can also be applied for the determination of WAD cyanide. In this process, prior to analysis, the sample is pretreated by means of ligand exchange to release cyanide from metal-cyanide complexes such as mercury, nickel, silver, and copper. The sample is then injected into the analyzer and acidified by means of hydrochloric acid (HCl) to convert cyanide to HCN. This is followed by the gas diffusion through the membrane into the receiving solution. In this alkaline solution, hydrogen cyanide is converted to cyanide ions. Finally, the ion concentration is determined amperometrically with the silver/silver electrode. The diagram of the system is shown in figure 12. (Mudder et al, 2001, pp.44-45)

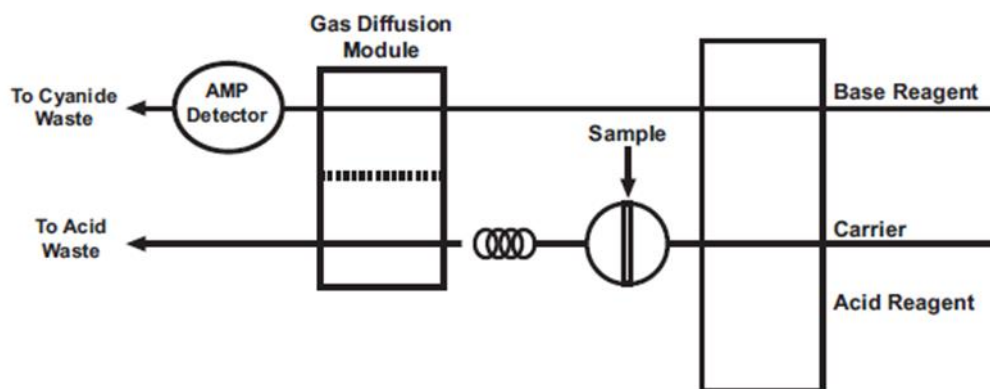


Figure 12. Schematic representation of FIA system for determination of WAD cyanide (EPA 2010b).

Sulistiyarti & Kolev (2013) studied the determination of WAD cyanides with online pretreatment coupled with flow injection analyzer and amperometric detection. The introduced ligand (combination of 0.10% thiourea and 0.10% pentaethylenhexamine) successfully liberated cyanide from the unstable and stable metal-cyanide complexes. The method provided fast analysis (60 samples per hour) of WAD compounds in samples with cyanide concentration ranging from 3 µg/liter to 10mg/liter. (Sulistiyarti & Kolev, 2013)

In conclusion, the Flow Injection Ligand Exchange (FILE) method is a promising technique for the determination of cyanide at concentrations in the range of 0.01-200 ppm. The analysis of higher concentrations requires thicker or multiple membranes. The main advantage of this technique is that thiocyanate does not produce *HCN* in the presence of NO_3^- . However, the presence of sulfide, carbonate, and chlorine can interfere with the precise determination directly or indirectly (see table 9). (Mudder et al, 2001, p.45; Young et al, 2008, p.733)

Table 9. The effects of interferences on the flow injection ligand exchange method and their elimination procedures (ASTM D6888-04; EPA 2010b; Young et al, 2008, p.733).

Interferences	Effects of interferences	Elimination of interferences
Sulfide ions	<p>The change of the electrode surface due to the formation of Ag_2S which causes an increase in the observed current.</p> <p>The acidified sulfide ions (H_2S) diffuse through the membrane and generate signals on the electrode surface (positive interference).</p> <p>Sulfide ions react with cyanide and reduce its concentration in the solution.</p>	The addition of bismuth nitrate instead of hydrochloric acid results in the precipitation and elimination of sulfide ions.
Carbonate	The released carbon dioxide from carbonate diffuses through the membrane and reduce the pH of the receiving solution.	Adding hydrated lime to the sample and allow the precipitation of $Ca(OH)_2/CaCO_3$.
Chlorine	Reacts with the silver electrode and oxidizes the cyanides.	Adding sodium arsenite or ascorbic acid to the sample before analysis.

3.4 Applying the alkaline solution of picric acid

Applying the alkaline solution of picric acid is a colorimetric technique for determining WAD cyanide concentration. This technique is based on the reaction of the picric acid with free cyanide from complexes such as nickel, zinc, cadmium, or copper-cyanide. The release of free cyanide from cyanide compounds can be carried out by means of diethylenetriamine penta-acetic acid (DTPA) or ethylenediaminetetraacetic acid (EDTA). In this process, the soluble alkali metal of picrate is transformed by cyanide to the isopurpuric acid (a salt with bright orange color). The intensity of the generated color is measured by spectrophotometer at the wavelength of 520 nm and evaluated by using its calibration curve. The intensity is directly related to WAD cyanide concentration. (Lipták & Venczel, 2016, p.271)

The maximum precision of the picric acid method for determining WAD cyanide is 0.26 mg/liter. The presence of SCN^- , CNO^- , and $S_2O_3^{2-}$, if their concentrations are 1230 mg/liter,

340 mg/liter, and 510 mg/liter, does not cause significant interferences. However, in the presence of sulfide ions, the sample should be treated by the addition of lead salts and consequent filtering (filtration is for removing the generated precipitates). (Woffenden et al, 2008, pp.88-89) Although this method is simple and relatively precise, it suffers from various drawbacks. As an instance, picric acid is explosive and requires special handling. Moreover, its application requires close control of its pH since the color development varies outside of the pH ranging from 9.0 to 9.5. (Cameron, 2002; Woffenden et al, 2008, p.89; Young et al, 2008, pp.733-734)

3.5 Ion selective electrode (ISE)

Another technique applied for the determination of free cyanide concentration is the electrochemical cell. This method consists of an ion selective electrode (ISE) along with a reference electrode, and a potential measuring device. The schematic diagram of this cell which analyses the concentration of samples based on the potentiometric measurement is depicted in figure 13. (Lindler & Pendley, 2013)

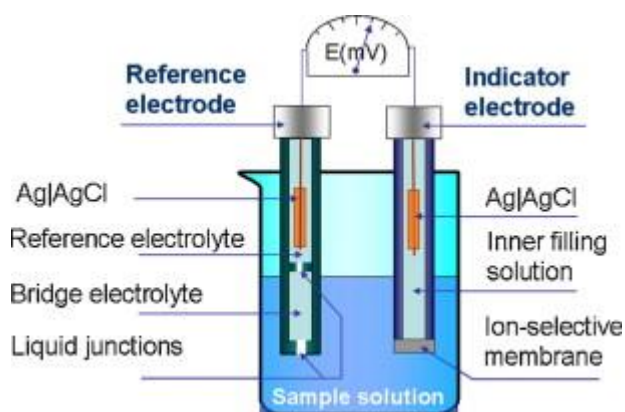


Figure 13. Schematic diagram of an electrochemical cell for potentiometric measurement (Lindler & Pendley, 2013).

ISE is principally a membrane-based device with an inner filling solution. The inner filling solution contains the ion of interest at the constant activity. When the electrode is immersed in the sample solution, the transportation of ions starts. The transportation occurs from the areas with high ion concentrations to the ones with low ion concentrations. The selective binding of ions with the specific sites of the membrane creates the potential difference which is directly proportional to the free cyanide concentration. (Wang, 2006, pp.165-166)

The ISE with the reference electrode and the potential measuring device is another applicable method for the analysis of samples with 0.5-10 ppm cyanide. In addition, this method can be applied after the distillation procedure for the measurement of WAD or total cyanide concentration. Advantages of ISE include its economic aspects, fast response, wide linear range, and its immunity to turbidity. The main drawback of this technique is that the existence of heavy metals, such as lead and mercury, in the solution may shorten the electrode life. However, the presence of bromide, thiosulfate, and thiocyanate, if their concentration is less than 10 ppm, does not cause significant interferences. (Young et al, 2008, p.734)

3.6 Amperometric method

Amperometric method is an electrochemical technique applicable for the determination of free cyanide concentration. An amperometric cell comprises of a working electrode, a reference electrode ($Ag/AgCl$ electrode), and a counter electrode (steel electrode). The working electrode can be glassy carbon, gold, or silver. However, the silver one is more common due to the properties such as its wide linear working range ($0.5\mu\text{g/liter}$ - 1gr/liter), long stability, low cost, and great reproducibility. The schematic representation of the amperometric cell is shown in figure 14. (Sulistiyarti et al, 1999)

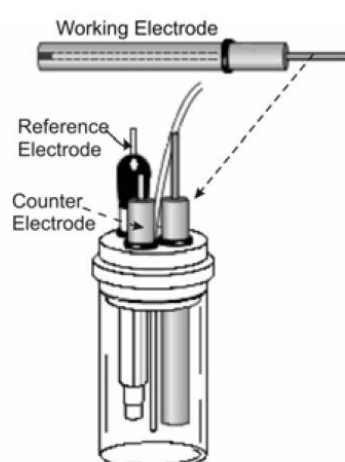


Figure 14. The schematic representation of the amperometric cell (Bojorge Ramírez et al, 2009).

In the analysis of the solution containing cyanide, the current generated during the reaction of the silver anode and cyanide anion (anodic polarization) is proportional to the concentration of cyanide, for clarification see reaction 17. (Barnes et al, 2000)



The main difficulties associated with the analysis of samples with the amperometric method is that the surfaces of the electrode expire with time. In addition, the reactions of other compounds in the solution with the working electrode result in the formation of numerous products. The adhesion of these products to the electrode surface prevent further reactions. The outcome of the abovementioned cases is decreasing the generated current and the height of the recorded peaks. Moreover, the coated or poisoned electrode surface may increase the noise and drift in the cell. In order to solve these problems, the addition of the appropriate standard, polishing or replacing the working electrode is suggested. This method is prone to error in the presence of sulfide, thiosulfate, metal-cyanide compounds, and oxidant. The effect of these interferences and the elimination procedure of them is described in table 10. (Robards, Haddad & Jackson 1994, pp.265-266; Young et al. 2008, p.734)

Table 10. The effect of interferences on amperometric method and their elimination procedure (Young et al, 2008, p.734).

Interferences	Effect of interferences	Elimination of interferences
Sulfide and thiosulfate	Formation of silver sulfide substrate on the electrode surface	Adding bismuth nitrate
Metals –cyanide compounds	Decreasing the diffusion current	–
Oxidant (ClO^- , H_2O_2)	Producing cathodic current	Adding arsenite or hydrazine

3.7 Chromatographic methods

The chromatographic methods for the determination of cyanide concentrations are high-performance liquid chromatography (HPLC), ion chromatography (IC), and gas chromatography (GC). Among these, IC is the most common method for cyanide determination. This technique includes size exclusion chromatography, ion-pair chromatography, and ion-exchange chromatography. (Nollet & De Gelder, 2007, p.730)

Giuriati et al. (2004) investigated the determination of CN^- and S^{2-} by ion chromatography. In this study, a two-potential waveform was adopted in order to eliminate the fouling of the silver-working electrode. The introduced eluent (0.4 M $NaOH$ and 7.5 mM oxalate solution) provided good selectivity and column efficiency. The reported detection limit in this study was 1.0 $\mu g/liter$ and 2.0 $\mu g/liter$ for sulfide and cyanide ion respectively. (Giuriati et al, 2004.) Destanoğlu and Gümüş Yilmaz (2016) studied the determination of cyanide ion and hexavalent chromium, $Cr(VI)$ via IC and conductivity detectors. The chloramine-T in alkaline pH and photo-oxidation followed by the addition of chloramine-T were applied to convert CN^- and metal-cyanide complexes to cyanate. They reported that this method can be applied for the determination of CN^- and $Cr(VI)$ in the linear range of 0.6-961.5 and 0.9-118.5 $\mu mol/liter$. The detection limit for the above-mentioned ions was 0.18 and 0.26 $\mu mol/liter$ respectively. (Destanoğlu & Gümüş Yilmaz, 2016)

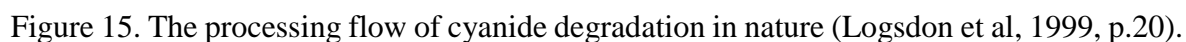
To sum up, ion chromatography is an accurate, reproducible and versatile method. The detection limit in pure and real mining solutions is 0.001 mg/liter and 0.05-0.5 mg/liter respectively. This technique can be applied for determining the metal- cyanide complexes of chromium, iron (II) and (III), gold, copper, cobalt, silver, and nickel. However, the method cannot determine the concentration of WAD in addition to total cyanide. (Mudder et al, 2001, p.44; Young et al, 2008, pp.734-735)

4 REMOVAL OF CYANIDE FROM WATER AND WASTEWATER

Free cyanide and its related compounds can be found in various industrial effluents. In order to make precautionary measures toward the health and environment, these effluents must be treated before discharge. The most common cyanide treatment methods include natural cyanide degradation, chemical treatment methods, biological cyanide degradation, and electrolytic degradation, which are described in the followings. (Kuyucak & Akcil, 2013.)

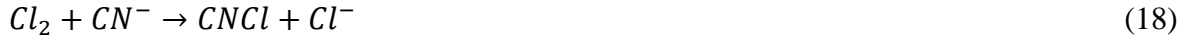
4.1 Natural degradation

In the natural degradation process, the cyanide solutions are detained in tails for a long period of time. The combination of natural, physical, biological, and chemical processes such as volatilization, chemical precipitation, photodecomposition, and microbial oxidation results

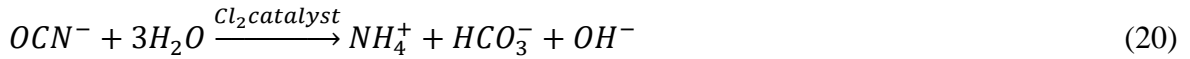


The chemical oxidation methods include alkaline chlorination, SO_2 /air process, iron/copper precipitation process, the hydrogen peroxide oxidation process, iron sulphide and sulphide precipitation, acidification process and cyanide recovery, and acidification-volatilization-regeneration processes. Alkaline chlorination is a well-known process to remove cyanide in

gold mining effluents. In this two-step process, the reaction of chlorine with cyanide results in the formation of $CNCl$. The hydrolysis of this compound in the next step yield cyanate (reactions 18 and 19). (Botz, 2001, p.4)



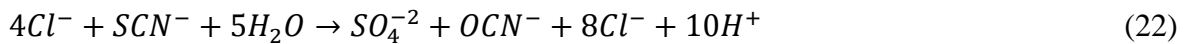
With the excess amount of chlorine, further hydrolysis of cyanate results in the formation of ammonia, as it is shown in reaction 20 (Botz 2001, p.4).



The sufficient amount of the excess chlorine leads to the complete oxidation of ammonia and formation of nitrogen gas according to reaction 21 (Botz, 2001, p.4).



In addition to cyanide removal, alkaline chlorination can also oxidize thiocyanate as it is shown in reaction 22 (Botz, 2001, p.4).



The main advantage of alkaline chlorination over SO_2 /air and the H_2O_2 process is that this method does not require copper as a catalyst. Moreover, the complexed metals with cyanide are precipitated as metal-hydroxide compounds at the end of the cyanide oxidation process. (Botz, 2001, p.5)

4.3 Electrocoagulation (EC) Method

Electrocoagulation method has received significant consideration in recent years due to its capability of treating different types of waters and wastewaters. In this process, the

introduced current to the cell results in the dissolution of sacrificial anodes, generation of cations, and their hydrocomplexes. Then the generated species act as destabilizer or coagulant agents and assist in the removal of contaminants from the solution (Garcia-Segura et al, 2017). The figure 16 represents the electrocoagulation unit that contains an electrolytic cell. In this cell, anode and cathode electrodes are connected to a DC power supply and submerged in polluted water (Marriaga-Cabrera & Machuca-Martínez 2014, p.6).

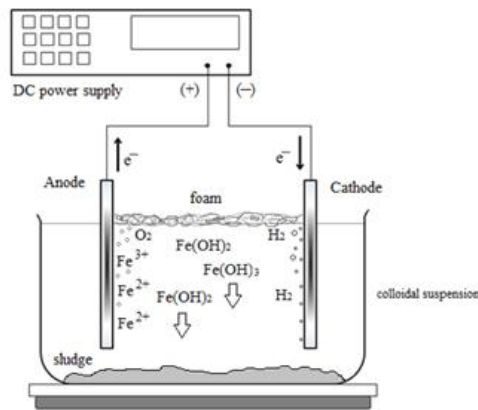
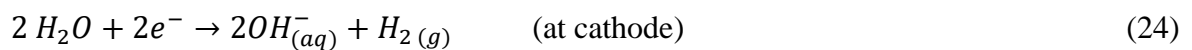


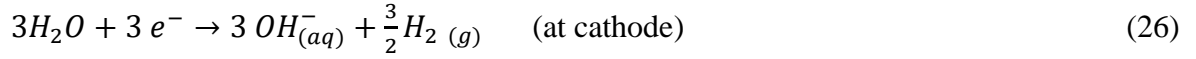
Figure 16. A schematic representation of the electrocoagulation system (Marriaga-Cabrera & Machuca-Martínez 2014, p. 6).

The removal of contaminants from the solution takes place in several stages. In the first step, which is known as anodic dissolution, the passage of the direct electric current results in the dissolution of the sacrificial anode and generation of metal cations. The aluminum and iron are the most commonly applied sacrificial anodes since they are accessible, reliable, and non-toxic. When iron is used as the sacrificial anode the reactions on the surface of the anode and cathode are according to reactions 23 and 24. (Garcia-Segura et al, 2017)

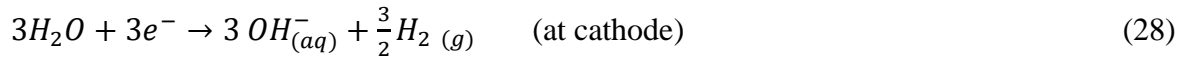


The other proposed mechanism for iron is shown in reaction 25 and 26 (Bazrafshan, Ownagh & Mahvi, 2012).





In case of using aluminum as the sacrificial anode, the following reactions take place (Bazrafshan et al, 2012).



In the subsequent step, the reaction of metallic cations and hydroxyl ions results in the generation of coagulants. The formation of these hydroxylated species, which are ion-complexes, is described in reactions 29 and 30. (Moussa et al, 2017.)



And for aluminum, the formation of hydroxylated species takes place according to reaction 31 (Bazrafshan et al, 2012).



The coagulants destabilize the contaminant, particulate suspensions, and break emulsions by three mechanisms consisting of compression of the electrical double layer, charge neutralization, and floc formation. In the compression of electrical double layer mechanism, the oxidation of the sacrificial anode produces the reverse charge ions within the solution. The counter charge ions penetrate the double layer and increase the ions concentration around the colloidal particles. This reduces the thickness of the electrical double layer and its repulsive forces. Hence, the colloidal particles gather around the electrode and form larger particles. (Comninellis & Chen, 2010, pp.245-246; Marriaga-Cabrales & Machuca-Martínez, 2014, p.9)

The other alternative mechanism is charge neutralization. In this mechanism, the counter charged ions are adsorbed onto the surface of the colloidal particles, which results in the neutralization of the surface charge. Later, the colloidal particles agglomerate each other and coagulate. The last mechanism is the floc formation mechanism in which the coagulation results in the formation of flocs, and these flocs generate a sludge blanket (Comninellis & Chen, 2010, pp. 245-246). The leftover particles within the aqueous medium can be captured or bridged through this sludge blanket (Marriaga-Cabrales & Machuca-Martínez, 2014, p.9). In the last step of the electrocoagulation process, the cathodic reaction produces hydrogen and in some cases oxygen bubbles. Next, these bubbles adhere to the coagulated species and rise the pollutants via natural buoyancy to the surface of the solution.

Numerous parameters affect the efficiency of electrocoagulation and its ability to remove contaminants from the solution. The most important ones from these parameters are electrode arrangement, type of power supply, current density, supporting electrolyte, pH, and electrode material. Regarding the electrode arrangement, the applied electrodes in the electrocoagulation cell can be either monopolar or bipolar. The configuration of these electrodes is depicted in figure 17. (Moussa et al, 2017)

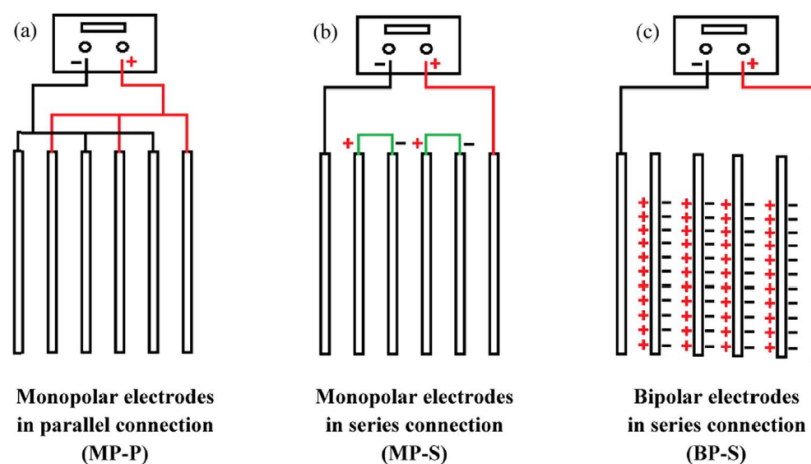


Figure 17. Different arrangement of electrode connection (Garcia-Segura et al, 2017).

The configuration of the electrodes is not the only determining factor for the pollutant's removal. In other words, parameters such as the nature of pollutants, the matrix of water, the current density, pH, and the electrode material can affect the elimination efficiency. However, the monopolar electrodes in a parallel connection (MP-P) are the cost-effective

configuration. On the other hand, the bipolar electrodes in a series connection (BP-S) require low maintenance and in some circumstances eases the pollutant removal. (Garcia-Segura et al, 2017; Moussa et al, 2017)

DC power supply is the most commonly applied source to provide an electric field in the EC cell. However, this power supply can lead to the formation of an impermeable oxide substrate on the surface of the cathode. The passivation of the cathode with this layer declines the ionic transfer and increases the resistance of the electrolytic cell. Hence, the dissolution of the sacrificial anode and the formation of hydroxylated species might be hampered directly or indirectly by the passivation. However, the addition of chloride ions can break this layer and improve the species formation. On the other hand, the AC power supplies with periodical energization can also guarantee a suitable electrode life by delaying the consumption of the electrodes. (Eyvaz, 2016; Moussa et al, 2017)

Another variable in the EC process is the current density that can be controlled directly through the process. This parameter ascertains several released metal ions during the anodic dissolution. The implementation of high current density increases the anodic dissolution. Furthermore, this parameter can also affect the dose of coagulants and the rate of hydrogen bubble generation on the electrode surface. However, this parameter is not completely independent, and factors such as pH, temperature, and water flow rate can influence the choice of the optimum value for the current density. (Moussa et al, 2017)

The presence of supporting electrolyte in the solution can prevent the migration effects and increase the conductivity of the solution. In addition, it reduces the ohmic drop and energy consumption. As an example, in the presence of sulfate, when the sacrificial anode is aluminum, the passivation of anode occurs. This occurrence is due to the high affinity of sulfide to generate complexes with aluminum. As another example, the presence of nitrate prevents the anodic dissolution of both iron and aluminum. In these cases, higher potential for the anodic dissolution should be applied to compensate the negative effects of the abovementioned problems. (Garcia-Segura et al, 2017)

Finally, pH and electrode material are the last two parameters, which are effective on the removal efficiency. The pH of the solution affects its conductivity and anodic dissolution.

However, as the pH of the solution varies during the process, finding the clear connection between pH and electrocoagulation efficiency is difficult (Moussa et al, 2017). The electrode material determines the reactions occurring during the electrocoagulation. Aluminum and iron are the preferred materials for the sacrificial anode since they are accessible, reliable and non-toxic. The anodic dissolution of iron can result in the formation of Fe^{+2} or Fe^{+3} . In comparison to Fe^{+3} , the lower positive charge of Fe^{+2} makes this ion a weaker coagulant. Regarding aluminum, it increases the removal efficiency according to some recent studies. Considering the characteristics of electrocoagulation, this method presents many advantages over the conventional treatment methods (Vepsäläinen et al, 2012). The advantages and disadvantages of this method are listed in table 11.

Table 11. Advantages and disadvantages of electrocoagulation process (Chaturvedi, 2013; Garcia-Segura et al, 2017; Marriaga-Cabrales & Machuca-Martínez, 2014, pp. 9-10; Moussa et al, 2017).

Advantages	More effective and faster separation of organic contaminants in comparison to the traditional coagulation.
	Easy to operate and automation.
	Insensitivity to pH values (except for extreme values).
	Low maintenance.
	Less sludge production in comparison to traditional coagulation.
	Stability, nontoxicity, and easily dewatering of the sludge.
	No secondary pollution.
	Ease of the pollutant collection from the surface of the solution.
	Easier floc separation (flocs are larger, more stable, acid resistant in comparison to the traditional method).
	The treated water is clear, fragrance-free and colorless with less Total Dissolved Solids (TDS).
Disadvantages	High rate of sacrificial anode consumption due to oxidation.
	High electricity consumption (which makes this process less economical in comparison to the traditional method).
	Requirement of post-treatment due to the presence of <i>Al</i> and <i>Fe</i> .
	Anode passivation and deposition of sludge on the electrodes limits the continuous operation mode.
	High levels of conductivity are required for the contaminated water.

Koby et al. (2010) studied the removal of cyanide from two different electroplating rinse water via the EC method. The pH, cadmium, and total concentration of cyanide in the cadmium electroplating rinse water were 8.6, 102 mg/liter, and 120 mg/liter respectively.

Regarding the nickel electroplating rinse water, the pH, nickel, and the total concentration of cyanide were 8, 175 mg/liter, and 261 mg/liter. They reported that EC process with the current density of about 30 A/m² and pH values of about 8-10 removed 99.4% and 99.9% of Cd^{+2} and CN^- in cadmium-cyanide solution. The current density of 60 A/m² and pH values of about 8-10 removed 99.1% and 99.8% of Ni^{+2} and CN^- from nickel-cyanide solution. (Koby et al, 2010)

Moussavi et al. (2011) investigated the cyanide removal from synthetic cyanide-laden wastewater with the EC process. Among the four different arrangement, the *Fe-Al* with the higher removal efficiency of about 90% was selected for treating the sample with 300 mg/liter cyanide and pH values of about 11.5. They reported that the cyanide removal increased from 43% to 91.8% after increasing the current density from 2 to 15 mA/cm². The cyanide removal at 15 mA/cm² and after aerating the tank increased from 45% to 98%. They succeeded to remove 100% cyanide in the continuous operation mode and at the hydraulic retention time of 140 min. The dominant removal mechanisms in this study were adsorption and complexation with iron hydroxides. (Moussavi et al, 2011)

Koby et al. (2017) studied the removal of cyanide from alkaline cyanide solution in the rinsing water of the electroplating industry. They reported that the pH value of about 9.5, the current density of 60 A/m² and operation time of 60 min in the EC cell can eliminate 99.9% of cyanide and 99.9% of zinc ions in a solution with 7.5-34 gr/liter zinc cyanide. (Koby et al, 2017)

EXPERIMENTAL PART

Several cyanide analysis methods were described in detail in the literature part. In this research, titration as a standard method and the most commonly applied technique in gold extraction industry was selected for the determination of cyanide concentrations. The objective of this study, the conducted experiments, and their results are discussed in this part.

5 THE OBJECTIVE

The main objective was to find out that what are the most important parameters in the determination of cyanide using the titration method. Moreover, how these parameters affect the accuracy of the results in the determination of free cyanide. The focus of the first and second series of experiments was to find the most reliable indicator for CN^- determination in the sodium cyanide solutions. Next, in the third series of experiments, the CN^- concentration was determined in synthetic mine water samples. The aim of this series was to propose a suitable analysis procedure for typical mining water samples. In this study, three series of experiments were conducted and the summary of them is presented in table 12.

Table 12. The summary of the conducted experiments in this study.

Item	The first series of experiments	The second series of the experiments	The third series of the experiments
Solution	Pure cyanide solution	Pure cyanide solution	Synthetic mine water
Solution concentration (ppm)	1, 5, 10, 50, 75, 100	1, 5, 10, 50, 75, 100	1, 10, 100
Titrant	Silver nitrate	Silver nitrate	Silver nitrate
Titrant concentrations (mol/liter)	0.01, 0.002, 0.001	0.00125, 0.000125, 0.0000125	0.00125, 0.000125
Indicator	Potassium iodide in the presence of ammonium hydroxide	p-dimethylaminobenzylidene rhodanine	p-dimethylaminobenzylidene rhodanine
Sample volumes (ml)	2, 5, 8	2, 5, 8	2, 5, 8
End-point	Permanent turbidity	Color change from yellow to pale pink	Color change from yellow to pale pink

6 MATERIALS AND METHODS

The applied chemicals, the required equipment, the preparation of titrant solutions, samples, indicators, and the formula for calculating cyanide concentration in each series of experiments are described in the following subsections.

6.1 Chemicals

A list of applied chemicals, their purities and manufacturers are presented in table 13.

Table 13. The chemicals used in this study.

Item No.	Chemical	Specification	Manufacturer
1	Acetone (CH_3COCH_3)	Molar mass: 58.08gr/mol, density: 0.79 gr/cm ³ (20°C)	Merck KGaA
2	Ammonium chloride (NH_4Cl)	Molar mass: 53.49 gr/liter, density: 1.53 gr/cm ³ (25°C), solubility: 372 gr/liter	Mallinckrodt Baker B.V
3	Ammonium hydroxide 25% (NH_4OH)	Density: 0.903 gr/cm ³ (20°C)	Merck KGaA
4	p-dimethylaminobenzylidene rhodanine ($C_{12}H_{12}N_2OS_2$)	Molar mass: 264.37 gr/mol, bulk density: 225 kg/m ³	Merck KGaA
5	Potassium iodide (KI)	Molar mass: 166.00 gr/mol, density: 3.23 gr/cm ³ (25°C)	Kebo Lab Ab
6	Silver nitrate solution ($AgNO_3$)	1 ampoule: for 1000 ml, c ($AgNO_3$): 0.1 mol/liter, density: 1.27 gr/cm ³ (20°C)	Merck KGaA
7	Sodium chloride ($NaCl$)	Molar mass: 58.44 gr/liter, density: 2.17 gr/cm ³ (20°C), solubility: 358 gr/liter	VWR
8	Sodium cyanide ($NaCN$)	Molar mass: 49.01 gr/mol, density: 1.6 gr/cm ³ (20°C), solubility: 370gr/liter	Merck KGaA
9	Sodium hydroxide ($NaOH$)	Molar mass: 40.00 gr/mol, density: 2.13 gr/cm ³ (20°C), solubility: 1090 gr/liter	Merck KGaA
10	Sodium nitrate ($NaNO_3$)	Molar mass: 84.99 gr/mol, density: 2.26 gr/cm ³ (20°C), solubility: 874 gr/liter	Merck KGaA
11	Sodium sulfate (Na_2SO_4)	Molar mass: 142.04 gr/mol, density: 2.70 gr/cm ³ (20°C), solubility: 200 gr/liter	Merck KGaA

6.2 Equipment

A list of required equipment for the experiments and their specifications is presented in table 14.

Table 14. The required equipment in this study.

Item No.	Equipment	Specification
1	Burette	Volume= 10 ml Accuracy= ± 0.02 ml
2	laboratory Clamp Stand	–
3	Erlenmeyer flask	Volume= 100 ml
4	Magnetic stirrer	Magnetic Stirrer VARIOMAG COMPACT
5	Magnetic stir bar	–
6	Volumetric flask	Flask No.1: 100 ml Accuracy= ± 0.10 ml Flask No.2: 500 ml Accuracy= ± 0.25 ml Flask No.3: 1000 ml Accuracy= ± 0.40 ml
7	Glass funnel	–
8	Glass rod	–

6.3 Preparation of the samples

For the first series of experiments, six different samples with the concentrations of 100, 75, 50, 10, 5, and 1 ppm CN^- were prepared from 1000 ppm CN^- solution. To keep the pH level of the sample higher than 10.5, 1 ml of 10 M $NaOH$ was added to each sample.

6.4 First series of the experiments

6.4.1 Preparation of the titrant

The stock solution of $AgNO_3$ (0.1 M) was prepared as follow:

1. Filling half of the 1000 ml volumetric flask with deionized water.
2. Dissolving an ampoule of $AgNO_3$ (manufactured by Merck) into the flask and shaking gently to mix the solution.
3. Filling the volumetric flask to its mark with deionized water.

The storage time for this solution was one month. In other words, the solution was prepared and used as a fresh one each month. This stock solution was used for the preparation of titrants with the concentrations of 0.010, 0.002, and 0.001 M $AgNO_3$.

6.4.2 Preparation of the indicators

There were two types of indicators in the first series of experiments. The first indicator was a 10% *KI* solution which was prepared as follows:

1. Adding of about 75 ml of deionized water into a 250 ml capacity beaker.
2. The gradual adding of 10 gr *KI* into the beaker through its sidewalls, while mixing it gently with a glass rod.
3. Transferring the prepared solution into a 100 ml volumetric flask, by using a glass funnel.
4. Rinsing the beaker and the funnel with a small amount of deionized water.
5. Filling of the volumetric flask to its mark with deionized water, and then shaking it gently to mix the solution.
6. Storing the prepared solution in a suitable container (the resultant solution is a 10% w/v solution).

The second indicator was a 10% *NH₄OH* which was prepared as follows:

- 1- Filling half of a 100 ml volumetric flask with deionized water.
- 2- Adding of about 40 ml of 25% *NH₄OH* solution to the flask by means of a measuring cylinder; then, shaking it gently to have a uniform solution.
- 3- Filling of the volumetric flask to its mark with deionized water.

6.4.3 The procedure of the experiment

The determination of free cyanide with *AgNO₃* as the titrant and *KI*, in the presence of *NH₄OH*, as the indicator was carried out according to the procedure from Kem Kyoto Electronics. This procedure consists of three steps:

1. Pipetting 2 ml of sample into a 100 ml Erlenmeyer flask.
2. Pipetting 2 ml of 10% *KI*.
3. Adding 3 ml of 10% *NH₄OH* by means of a measuring cylinder.

After rinsing the flask's wall with deionized water and filling the burette with *AgNO₃*, the sample was titrated until its permanent turbidity which was easy to observe. To have a better observation, the flask was placed on a black sheet during the titration. The analysis of each sample was repeated five times and the same procedure was also carried out with 5 ml and

8 ml samples. The end-point of the procedure is shown in figure 18. (Kem Kyoto Electronics, 2018.)

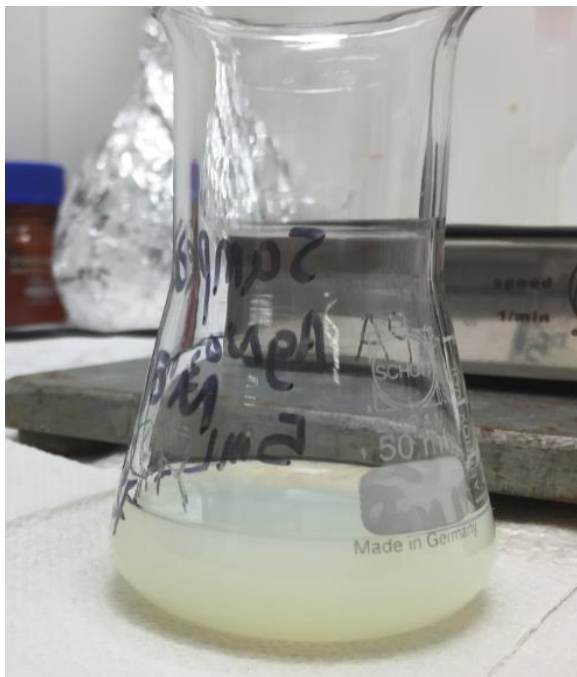


Figure 18. The end-point of the titration with AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator.

6.4.4 Formulas

The free cyanide concentrations were calculated using the following formula from a catalog known as free cyanide in silver plating solution, precipitation titration by automatic potentiometric titrator from KEM Kyoto Electronics (KEM Kyoto Electronics, 2018).

$$\text{Concentration of free cyanide (ppm)} = (EP1 - BL1) \times TF \times C1 \times K1 / \text{SIZE} \quad (32)$$

where EP1 is the titration volume in ml, BL1 is the blank level at 0.0 ml, TF is the dimensionless coefficient known as the factor of reagent, K1 is the constant conversion coefficient to convert gr/liter to ppm and is 1000, SIZE is the sample volume in ml; and, finally, C1 is the concentration conversion coefficient which can be calculated from equations 33 to 35:

$$1 \text{ ml } AgNO_3 \times \frac{1 \text{ lit}}{1000 \text{ ml}} \times \frac{0.1 \text{ mole}}{\text{lit}} = 0.0001 \text{ mole } AgNO_3 \quad (33)$$

According to the following reaction 1 mole $AgNO_3$ can react with 2 moles of KCN :



Then, C1 can be calculated using the equation 35:

$$0.0002 \text{ mole } KCN \times 65.12 \frac{\text{gr}}{\text{mol}} KCN \times \frac{1000 \text{ mg}}{1 \text{ gr}} = 13.024 \text{ mg } KCN \text{ per } 1 \text{ ml of } AgNO_3 \quad (35)$$

The abovementioned equations can be used when KCN is used for sample preparation. However, in this study, $NaCN$ was utilized to prepare the samples. Thus, equation 36 is the suitable formula for the calculation in this study.

$$\text{Concentration of free cyanide (ppm)} = (EP1 - BL1) \times 1.008 \times 9.802 \times K1/SIZE \quad (36)$$

Equation 36 can be used for the calculation of free cyanide concentration where the applied titrant is 0.1 M $AgNO_3$. For the 0.010, 0.002, and 0.001 M $AgNO_3$, the factor of reagent and the concentration conversion coefficient are listed in table 15.

Table 15. The factor of reagent and concentration conversion coefficient in the determination of cyanide with $AgNO_3$ as titrant and KI in the presence of NH_4OH as an indicator.

Titrant (mol/liter)	Factor of reagent	Concentration conversion coefficient (1 mg $NaCN$ per 1 ml of $AgNO_3$)
0.010 (10 times diluted)	$\frac{1.008}{10} = 0.10080$	0.98020
0.002 (50 times diluted)	$\frac{1.008}{50} = 0.02016$	0.19600
0.001 (100 times diluted)	$\frac{1.008}{100} = 0.01008$	0.09802

6.5 Second series of the experiments

6.5.1 Preparation of the titrant

In the second series of experiments, 0.1 M solution of $AgNO_3$ was prepared in the same manner as introduced in section 6.4.1. The analysis of the samples in this series was performed with three different concentrations of the $AgNO_3$, which were 0.0012500, 0.0001250, and 0.0000125 M.

6.5.2 Preparation of the indicator

The applied indicator in this part was p-dimethylaminobenzylidene rhodanine which was prepared as follows:

1. Adding of about 0.03 gr of the p-dimethylaminobenzylidene rhodanine powder.
2. Dissolving the powder in 100 ml acetone.
3. Storing the solution in a dark bottle.

6.5.3 The procedure of the experiment

The determination of free cyanide with $AgNO_3$ as the titrant and rhodanine as the indicator was firstly studied by Ryan and Culshaw (1944). Here, the utilized modified method is as following:

1. Pipetting 2 ml of the sample liquid into a 100 ml Erlenmeyer flask.
2. Adding 4 drops of rhodanine.

After rinsing the flask wall with deionized water and filling the burette with $AgNO_3$, the sample was titrated until its color changed from yellow to pale pink. The analysis of each sample was repeated five times and the same process was carried out on the samples with volumes of 5 ml and 8 ml. The end-point of the titration process is shown in figure 19. These samples were prepared in the same manner as the procedure introduced in section 6.3.

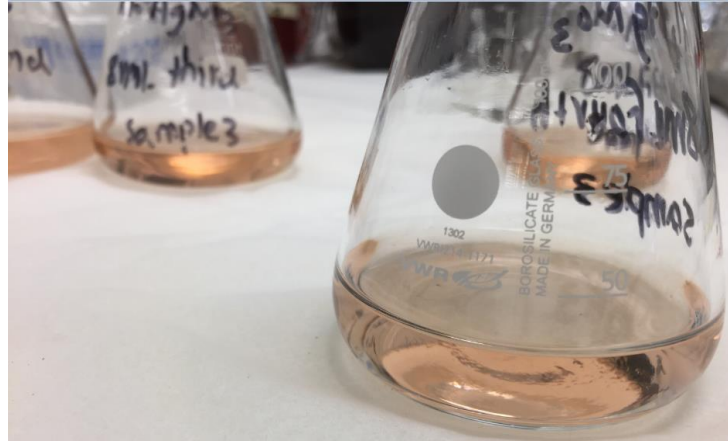


Figure 19. The end-point of the titration with AgNO_3 as the titrant and rhodanine as the indicator.

6.5.4 Formulas

The concentration of free cyanide in the solution was calculated in the second series of experiments using equations 37 and 38 from Geological Survey of Finland (GTK) (2009, pp. 1-2).

$$\text{NaCN (ppm)} = \frac{V_{\text{AgNO}_3}}{V_{\text{sample}}} \times \text{factor of reagent} \times 10000 \quad (37)$$

$$\text{CN}^- (\text{ppm}) = \text{NaCN (ppm)} \times \frac{26.09 \frac{\text{gr}}{\text{mol}} \text{NaCN}}{49.01 \frac{\text{gr}}{\text{mol}} \text{CN}^-} \quad (38)$$

Where V_{AgNO_3} and V_{sample} are the volumes of the titrant and the sample in ml. Adding 25 ml of 0.1 M AgNO_3 to 200 ml deionized water gave 0.0125 M AgNO_3 . For this case, the factor was 0.12255. Regarding 10, 100, and 1000 times diluter titrant with the concentration of 0.0012500, 0.0001250, and 0.0000125 M AgNO_3 , the factor of reagent is divided by 10, 100, and 10000. In this case for the abovementioned AgNO_3 solutions, the factor of reagent is 0.01225500, 0.00122550, and 0.00012255 respectively.

6.6 Third series of the experiments

The third series of experiments was conducted to determine the free cyanide concentrations in synthetic mine water. For this purpose, based on the discussion in section 7.1.2 and 7.2.2, rhodanine as the most reliable indicator was selected. The most suitable titrant concentrations for the determination of specific cyanide concentrations were selected based on the second series of experiments that are summarized in table 31. In this series, the titrant and the indicator were prepared in the same way as explained in sections 6.5.1 and 6.5.2.

After the preparation of the titrant and indicator, the stock solution of synthetic mine water containing 10000 ppm sulfate (SO_4^{2-}), 100 ppm nitrate (NO_3^-), 150 ppm ammonium (NH_4^+), and 1000 ppm chloride Cl^- was prepared as followings:

1. Filling half of the 1 liter volumetric flask with deionized water.
2. Dissolving of about 14.787 gr sodium sulfate (Na_2SO_4), 0.137 gr sodium nitrate ($NaNO_3$), 0.445 gr ammonium chloride (NH_4Cl) and 1.162 gr sodium chloride ($NaCl$).
3. Filling of the volumetric flask to mark with deionized water.

Finally, three samples were prepared as follows:

1. Adding 10 ml of synthetic mine water (stock solution) to the 100 ml volumetric flask.
2. Adding the required volume of 1000 ppm CN^- (0.1 ml, 1 ml, and 10 ml to have 1 ppm, 10 ppm, and 100 ppm cyanide solutions).
3. Adding 1 ml of 10 M $NaOH$ to keep the pH to values above 10.5.
4. Filling of the volumetric flask to mark with deionized water.

Three samples with the concentration of 1, 10, 100 ppm free cyanide were prepared. Each sample included 1000 ppm SO_4^{2-} , 10 ppm NO_3^- , 15 ppm NH_4^+ , and 100 ppm Cl^- .

7 RESULTS AND DISCUSSIONS

In all series of the experiments, the free cyanide concentration was determined in 2 ml, 5 ml, and 8 ml sample volume; in addition, each sample was titrated 5 times. In order to find the optimum titrant concentration for the analysis of specific cyanide concentration, some

samples were titrated with two or three different concentrations of $AgNO_3$. The results of each series of the experiments are presented and discussed in the following sections subsequently.

For each experiment, the calculated concentrations and errors are presented by using a box plot. A box plot is a graphical method of displaying variation in a set of data. This plot is a suitable way of visually presenting the data distribution via their quartiles. The lines extending parallel from the boxes are known as the “whiskers”, which are used to indicate variability outside the upper and lower quartiles (see figure 20). The main advantage of this graph is taking up less space, which is convenient for comparing the distributions between many datasets. The types of explanations from observing a box plot are:

1. What the key values are, such as the average, median 25th percentile etc.
2. If there are any outliers and what their values are.
3. Is the data symmetrical?
4. How tightly is the data grouped?
5. If the data is skewed and if so, in what direction.

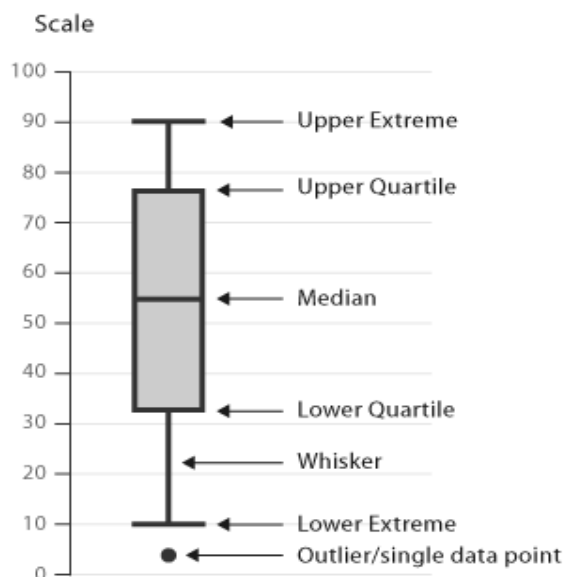


Figure 20. The anatomy of a box plot (Ribecca, 2015).

7.1 Results and discussion of the first series of experiments

In the first series of experiments, the cyanide concentration was determined in 6 samples containing 100, 75, 50, 10, 5, 1 ppm free cyanide. The analysis of 100 ppm cyanide solution was conducted using 0.010 AgNO_3 . The box plot from the achieved data for this sample is presented in figure 21. In addition, table 16 is presented to show the average concentrations, standard deviations, and errors resulting from titration.

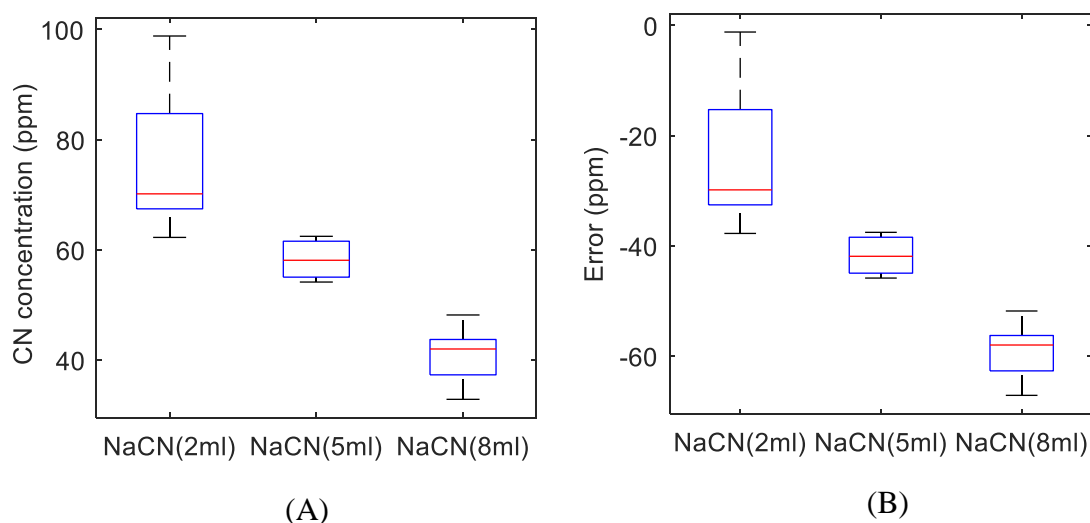


Figure 21. Results from the titration of 100 ppm cyanide solution with 0.010 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 16. The average concentrations, standard deviations, average errors, and % errors in the titration of the 100 ppm cyanide solution with 0.010 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator.

Sample volume (ml)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	76.07	14.19	-23.92	-23.92
5	58.25	3.60	-41.74	-41.74
8	40.80	5.59	-59.19	-59.19

As can be seen in figure 21, the standard deviation of the obtained concentrations in the titration of 5 ml cyanide solution is very low (3.60 ppm). Also, in the analysis of 8 ml solution the low deviation can be observed (5.59 ppm). However, the average of the obtained concentrations which were 58.25 ppm and 40.80 ppm was lower than the expected

concentration of 100 ppm. Although in the analysis of 2 ml sample volume, the error was lower, the average of the obtained concentrations is still lower than 100 ppm. Based on this it can be clearly seen that *KI* in the presence of NH_4OH as the indicator and 0.010 M $AgNO_3$ cannot determine 100 ppm free cyanide in this sodium cyanide solution.

The analysis of 75 ppm cyanide solution was conducted using the same $AgNO_3$ concentration. The achieved data for this sample is presented in figure 22 and table 17.

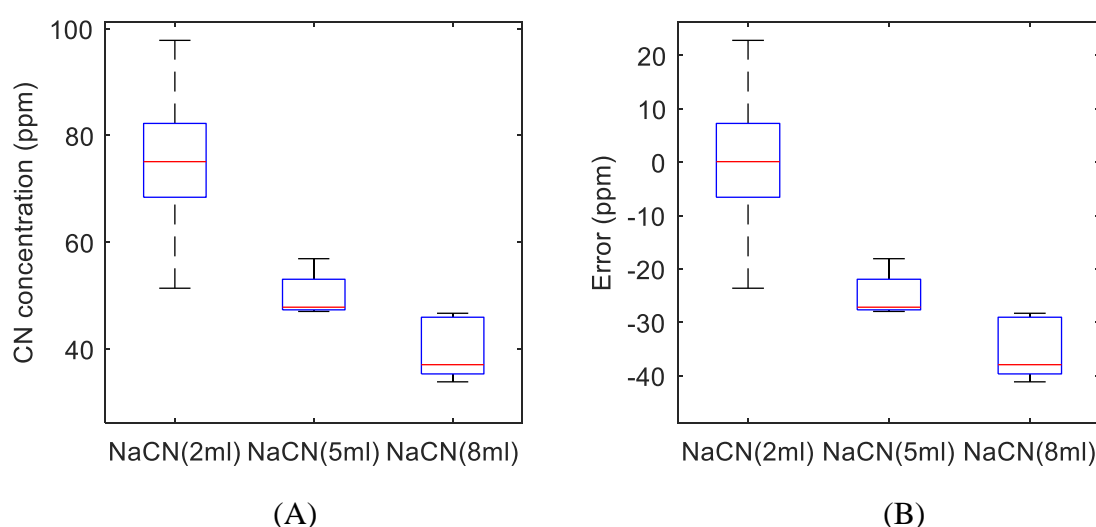


Figure 22. Results from the titration of 75 ppm cyanide solution with 0.010 M $AgNO_3$ as titrant and *KI* in the presence of NH_4OH as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 17. The average concentrations, standard deviations, average errors, and % errors in the titration of the 75 ppm cyanide solution with 0.010 M $AgNO_3$ as titrant and *KI* in the presence of NH_4OH as the indicator.

Sample volume (ml)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	75.09	16.45	0.09	0.12
5	50.19	4.21	-24.80	-33.07
8	39.81	5.93	-35.18	-46.90

As can be seen in table 17, the standard deviation in the obtained data in the analysis of 5 ml and 8 ml sample volume was low (4.21 ppm and 5.93 ppm). However, the average of the obtained concentrations (50.19 ppm and 39.81 ppm) was lower than the expected

concentrations of 75 ppm. But *KI* in the presence of NH_4OH as the indicator, the 0.010 M $AgNO_3$, and the sample volume of 2 ml could successfully determine 75 ppm free cyanide in this sample.

The obtained results in the titration of 50 ppm cyanide solution are presented in figure 23 and table 18. The free cyanide concentration in this sample was determined using 0.010 M $AgNO_3$.

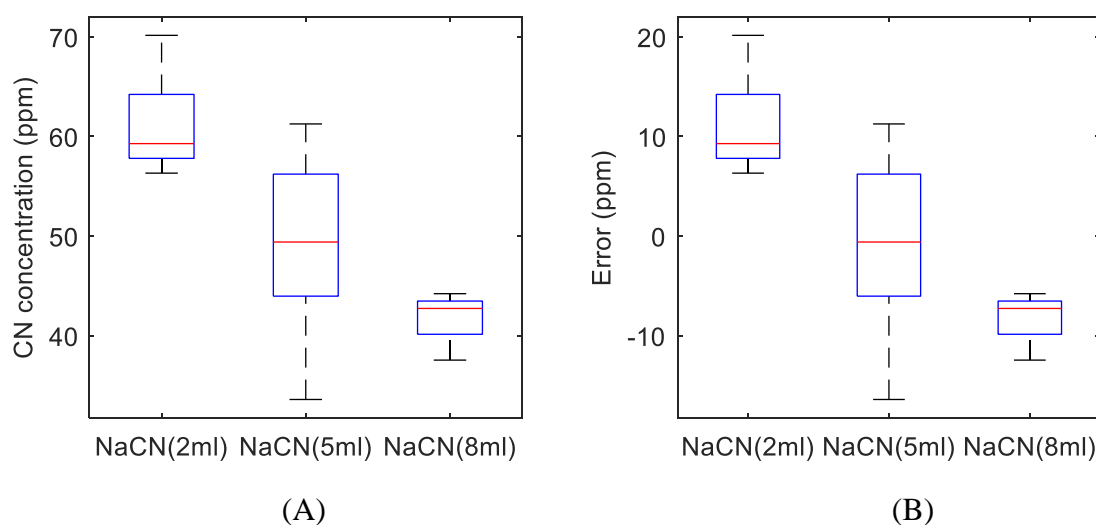


Figure 23. Results from the titration of 50 ppm cyanide solution with 0.010 M $AgNO_3$ as titrant and *KI* in the presence of NH_4OH as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 18. The average concentrations, standard deviations, average errors, and % errors in the titration of the 50 ppm cyanide solution with 0.010 M $AgNO_3$ as titrant and *KI* in the presence of NH_4OH as the indicator.

Sample volume (ml)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	61.25	5.41	11.25	-22.51
5	49.24	10.25	-0.75	-1.51
8	41.74	2.61	-8.25	-16.51

As can be seen in table 18, the average of the obtained concentrations in the analysis of 2 ml sample volume which is 61.25 ppm was higher than the expected concentration. On the other hand, in the analysis of 8 ml sample volume, the average concentration of about 41.74 ppm was lower than 50 ppm. Therefore, the applied indicator, the 0.010 M $AgNO_3$, and 5 ml

sample volume with the lowest error of about -0.75 ppm was the best option for the determination of 50 ppm free cyanide in this solution.

For the sample with 10 ppm cyanide concentration, three different titrants consisting of 0.002, 0.001, and 0.010 M AgNO_3 were evaluated to find the best titrant for the analysis. Based on table 19 and table I-1 in appendix I, 0.002 M AgNO_3 with the lowest error which varies from - 4.90 ppm to -6.49 ppm was the best option regarding this experiment. Thus, further analyses were carried out using this titrant. The results of 10 ppm CN^- sample using 0.002 M solution are shown in figure 24. In addition, table 19 presents average concentrations, standard deviations, average errors, and % errors from the analysis with 0.002 M AgNO_3 . The results of the other two applied AgNO_3 solution are presented in table I-1 appendix I.

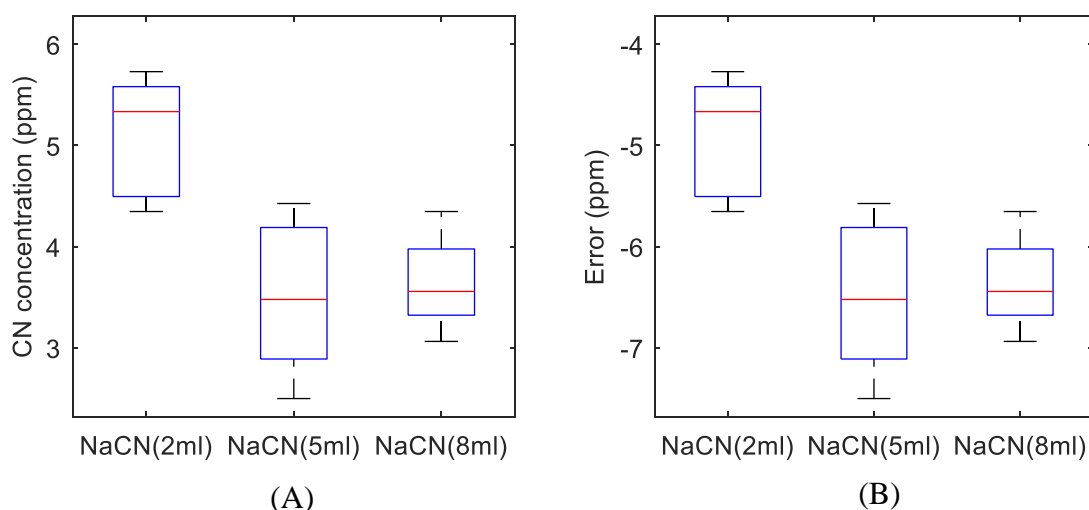


Figure 24. Results from the titration of 10 ppm cyanide solution with 0.002 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 19. The average concentrations, standard deviations, average errors, and % errors in the titration of the 10 ppm cyanide solution with 0.002 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator.

Sample volume (ml)	Titration concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	0.002	5.09	0.61	-4.90	-49.03
5	0.002	3.50	0.78	-6.49	-64.95
8	0.002	3.64	0.48	-6.35	-63.55

Based on table 19 and table I-1 in appendix I, the 0.002 M AgNO_3 , showed the lowest error of about -64.95% in comparison to the other applied titrants in the analysis of 5 ml cyanide solution (97.6% in the analysis with 0.010 M AgNO_3 , and -83.5% in the analysis with 0.001 M AgNO_3 . However, the average of the obtained concentrations of about 5.09 ppm, 3.50 ppm, and 3.64 ppm in the analysis of 2ml, 5ml, and 8 ml was lower than the expected concentration. Hence, the 0.002 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator cannot determine 10 ppm free cyanide in the cyanide solution.

Regarding the sample with 5 ppm cyanide concentration, two different titrants consisting of 0.001 and 0.002 were evaluated. Based on table 20 and table I-2 in appendix I, the 0.002 M AgNO_3 showed the lower error of about -2.07 ppm in the analysis of 5 ml cyanide solution (the error in the analysis with 0.001 M AgNO_3 was -3.56 ppm). The results of the analysis 5 ppm cyanide solution using the 0.002 M solution are shown in figure 25. In addition, table 20 presents average concentrations, standard deviations, average errors, and % errors from the analysis with 0.002 M AgNO_3 . The results of the other applied AgNO_3 solution are presented in table I-2 appendix I.

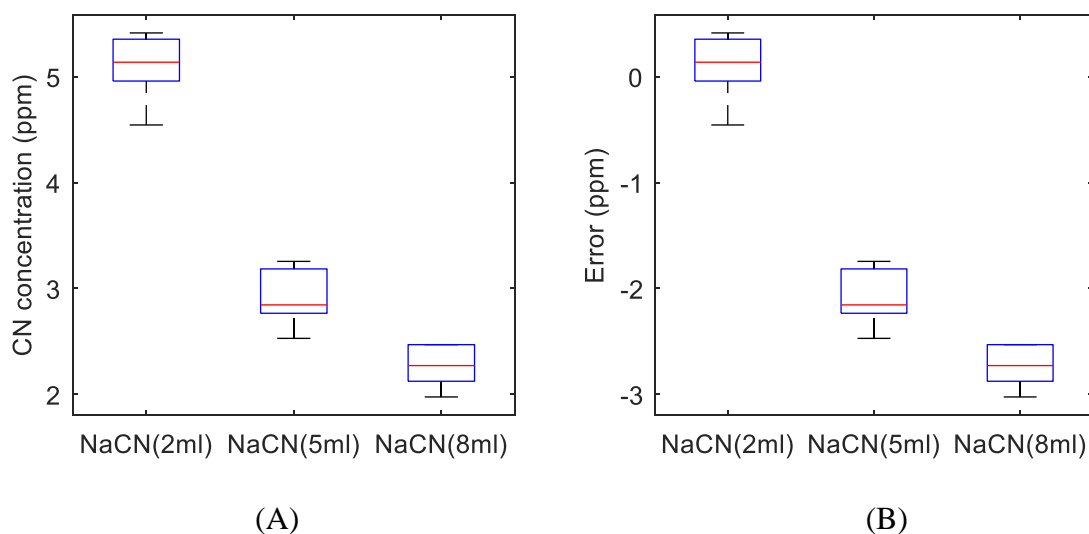


Figure 25. Results from the titration of 5 ppm cyanide solution with 0.002 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 20. The average concentrations, standard deviations, average errors, and % errors in the titration of the 5 ppm cyanide solution with 0.002 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator.

Sample volume (ml)	Titrant concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	0.002	5.10	0.34	0.10	2.1
5	0.002	2.92	0.28	-2.07	-41.46
8	0.002	2.27	0.20	-2.72	-54.56

As can be seen in figure 25, the variation of data in the analysis 2 ml, 5 ml, and 8 ml sample volume was very low (0.34 ppm, 0.28 ppm, and 0.20 ppm). However, according to table 20, only the analysis of 2 ml sample volume with 0.002 M AgNO_3 as titrant and KI in the presence of NH_4OH could successfully determine 5 ppm free cyanide in the cyanide solution.

Finally, the 1 ppm cyanide solution was titrated with 0.002 and 0.001 M AgNO_3 . Based on table 21 and table I-3 in appendix I, the 0.001 M AgNO_3 showed the lower error of about -17.1% in the analysis of 5 ml cyanide solution (the error in the analysis with 0.002 M AgNO_3 was 192%). The results of the analysis 1 ppm cyanide solution using the 0.001 M solution are shown in figure 26. In addition, table 21 presents average concentrations, standard

deviations, average errors, and % errors from the analysis of this sample. The results of the other applied AgNO_3 solution are presented in table I-3 appendix I.

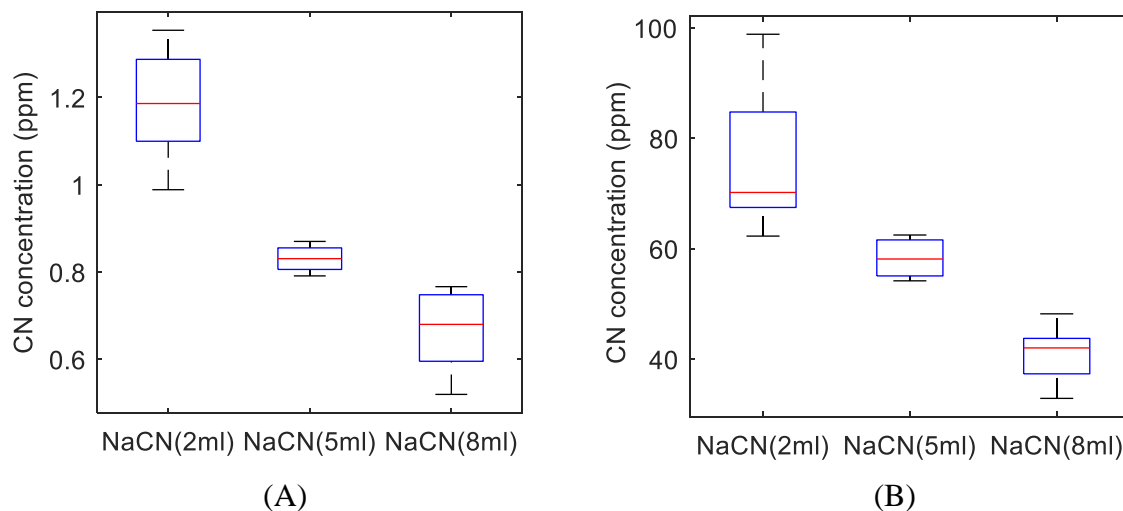


Figure 26. Results from the titration of 1 ppm cyanide solution with 0.001 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 21. The average concentrations, standard deviations, average errors, and % errors in the titration of the 1 ppm cyanide solution with different titrants with 0.001 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator.

Sample volume (ml)	Titrant concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	0.001	1.18	0.13	0.18	18.5
5	0.001	0.82	0.03	-0.17	-17.1
8	0.001	0.66	0.09	-0.33	-33.6

As can be seen in figure 26, the standard deviation of data in the analysis of 5 ml sample volume was very low in comparison to the other sample volumes (0.03 ppm). However, according to table 21, this titrant could determine approximately 1 ppm free cyanide in the analysis of 2 ml sodium cyanide solution.

7.1.1 The optimum concentrations of titrant

In the analysis of 2 ml sample volume, the magnetic stir bar due to the low sample volume did not rotate properly. On the other hand, in the analysis of 8 ml sample volume, the visual

detection of samples with the final volume of approximately 10.66 ml and 16.80 ml was difficult. Thus, the 5 ml sample volume was selected for the analysis of cyanide in aqueous solutions. Regarding the optimum concentrations of titrant for the analysis of cyanide in solutions containing 1-100 ppm free cyanide, table 22 summarize the applied and the best AgNO_3 for each sample.

Table 22. Samples and their most suitable titrant in the determination of cyanide with KI and NH_4OH as the indicator.

Sample concentration (ppm)	Sample volume (ml)	Titrant		
		0.010 M AgNO_3	0.002 M AgNO_3	0.001 M AgNO_3
100	5	✓	–	–
75	5	✓	–	–
50	5	✓	–	–
10	5	×	✓	×
5	5	–	✓	×
1	5	–	×	✓
✓ Minimum error × Unacceptable – Not tested				

Regarding 100 ppm cyanide solution (see table 16), it can be observed that 0.010 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator cannot determine free cyanide concentration in this sample. Regarding 75 ppm and 50 ppm cyanide solution (see table 17, table 18), the 0.010 M AgNO_3 successfully determined free cyanide in 2 ml sample volume with the average error of about 0.12% in the first cyanide solution. About the 50 ppm cyanide solution, the 0.010 M AgNO_3 determined free cyanide in 5 ml sample volume with the average error of -1.51%.

Regarding the 10 ppm cyanide solution (see table 19 and table I-1 in appendix I), although the 0.002 M AgNO_3 showed the lowest error in comparison to the other titrants, it could not determine the expected concentration. Concerning the 5 ppm cyanide solution (see table 20), the 0.002 M AgNO_3 could determine the expected concentration in 2 ml sample volume; The reported error in this sample was only 2.1%. Finally, regarding 1 ppm cyanide solution (see table 21), the 0.001 M AgNO_3 with the average error of about 0.18 ppm could determine approximately 1 ppm free cyanide in 2 ml sample volume.

As can be seen in table 16 to table 21, by increasing the sample volume the standard deviation decreased. Although in table 18 to table 19, first the standard deviation was increased, in the analysis 8 ml sample volume, the deviation decreased again. This can be explained in this way that at higher sample volume the accuracy of the obtained data was better, and this could be due to the easiness in the detection of turbidity at 8 ml sample volume.

7.1.2 The reliability of the indicator

Considering the best sample size and titrant concentration, results showed that *KI* in the presence of *NH₄OH* is not a reliable indicator to determine *CN* in the sodium cyanide solution. Hence, this method can clearly be rejected for the analysis of cyanide in aqueous solutions. Finally, the applied *AgNO₃* concentrations, standard deviations, average error, and the % error in the analyzed samples are presented in table 23.

Table 23. The numerical results achieved from the titration of 5 ml cyanide solutions with *AgNO₃* as titrant and *KI* in the presence of *NH₄OH* as the indicator.

Sample concentration(ppm)	Titrant concentration (mol/liter) <i>AgNO₃</i>	Standard deviation (ppm)	Average error (ppm)	Average error (%)
100	0.010	3.60	-41.74	-41.74
75	0.010	4.21	-24.80	-33.07
50	0.010	10.25	-0.75	-1.51
10	0.002	0.78	-6.49	-64.95
5	0.002	0.28	-2.07	-41.46
1	0.001	0.03	-0.17	-17.10

7.2 Results and discussion of the second series of experiments

In the second series of experiments, the cyanide concentration was determined in 6 samples containing 100, 75, 50, 10, 5, 1 ppm free cyanide. The determination of cyanide was conducted using *AgNO₃* as titrant and rhodanine as the indicator. The analysis of 100 ppm cyanide solution was conducted using 0.0012500 M *AgNO₃*. The box plot from the achieved data for this sample is presented in figure 27. In addition, table 24 is presented to show the average values, standard deviations, and errors during titration.

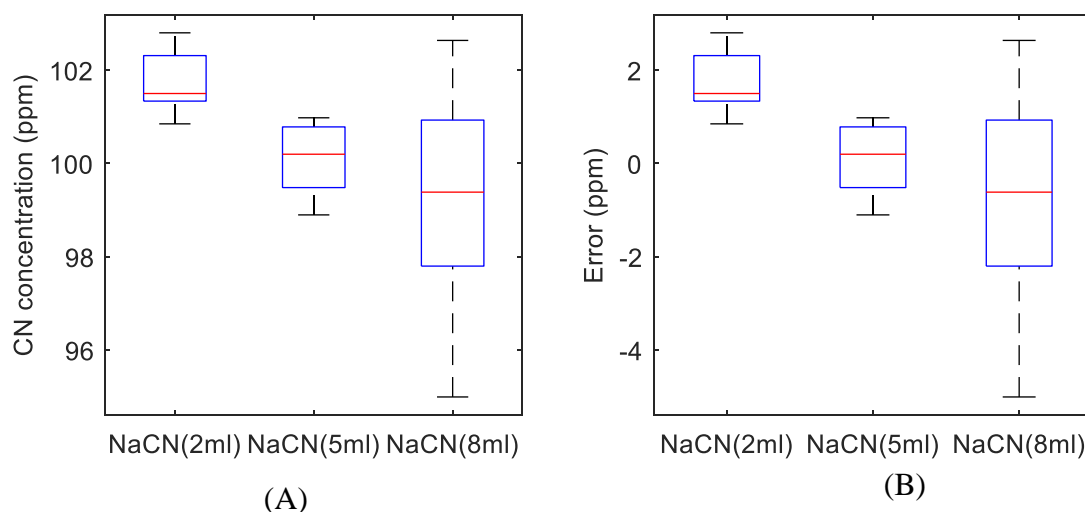


Figure 27. Results from the titration of 100 ppm cyanide solution with 0.0012500 M AgNO_3 and rhodanine as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 24. The average concentrations, standard deviations, average errors, and % errors in the titration of the 100 ppm cyanide solution with 0.0012500 M AgNO_3 as titrant and rhodanine as the indicator.

Sample volume (ml)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	101.75	0.74	1.75	1.75
5	100.09	0.83	0.09	0.09
8	99.22	2.78	-0.77	-0.77

As can be seen in figure 27, the standard deviation in the analysis of 2 ml and 5 ml sample volume was low (0.74 ppm and 0.83 ppm). Among these two tests, the 0.0012500 M AgNO_3 as titrant and rhodanine as the indicator could successfully determine 100 ppm free cyanide in 5 ml cyanide solution. According to table 24, the error in the analysis was only 0.09 ppm.

The analysis of 75 ppm cyanide solution was conducted using the same AgNO_3 concentration. The achieved data for this sample is presented in figure 28 and table 25.

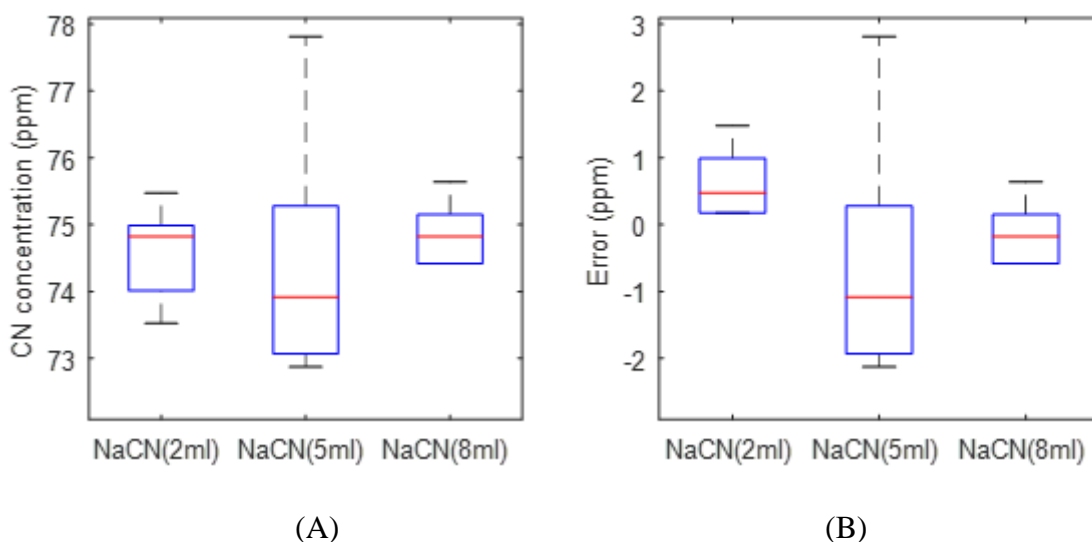


Figure 28. Results from the titration of 75 ppm cyanide solution with 0.0012500 M AgNO_3 and rhodanine as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 25. The average concentrations, standard deviations, average errors, and % errors in the titration of the 75 ppm cyanide solution with 0.0012500 M AgNO_3 as titrant and rhodanine as the indicator.

Sample volume (ml)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	74.56	0.74	-0.43	-0.58
5	74.43	1.99	-0.56	-0.75
8	74.69	0.90	-0.30	-0.41

As can be seen in table 25, the analysis of 2 ml, 5 ml, and 8 ml cyanide solution determined approximately the expected concentration. Hence, the 0.0012500 M AgNO_3 as titrant and rhodanine as the indicator can be applied for the determination of free cyanide in 75 ppm cyanide solution in all the sample volumes mentioned in the table.

The obtained results in the titration of 50 ppm cyanide solution are presented in figure 29 and the table 26. The free cyanide concentration in this sample was determined using 0.0012500 M AgNO_3 .

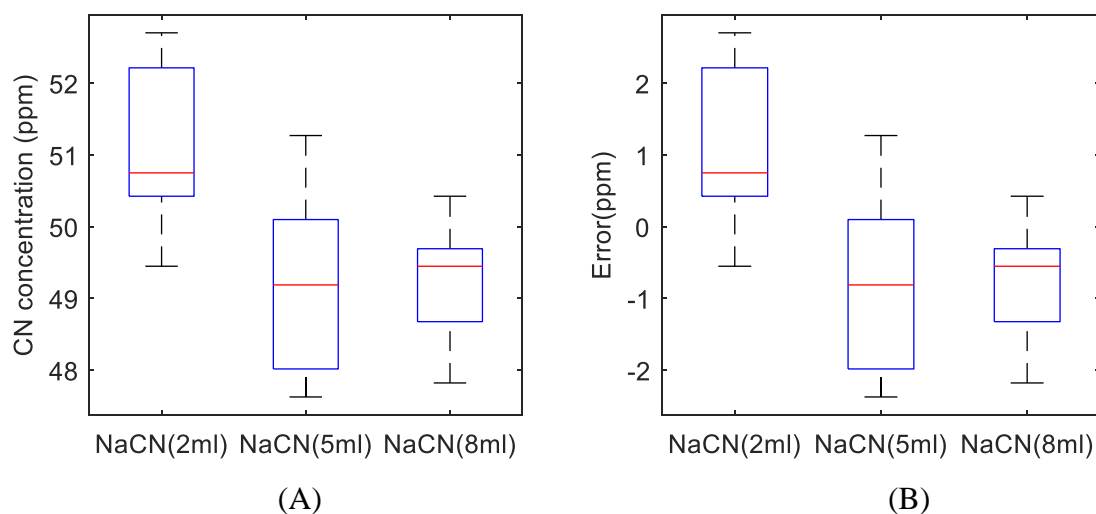


Figure 29. Results from the titration of 50 ppm cyanide solution with 0.0012500 M AgNO_3 and rhodanine as the indicator: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 26. The average concentrations, standard deviations, average errors, and % errors in the titration of the 50 ppm cyanide solution with 0.0012500 M AgNO_3 as titrant and rhodanine as the indicator.

Sample volume (ml)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	51.13	1.26	1.139	2.27
5	49.18	1.42	-0.81	-1.62
8	49.22	0.94	-0.77	-1.56

As can be seen in table 26, the average of the obtained concentrations in the analysis of 2 ml sample volume which is 51.13 ppm was higher than the expected concentration. On the other hand, in the analysis of 5 ml sample volume, the average concentration of about 49.18 ppm was lower than 50 ppm. Therefore, the 0.0012500 M AgNO_3 as the titrant, rhodanine as the indicator, and 8 ml sample volume with the lowest error of about -0.77 ppm were the best option for the determination of 50 ppm free cyanide in this solution.

Regarding the sample with 10 ppm cyanide concentration, the 0.0012500 M AgNO_3 and 0.0001250 M AgNO_3 were evaluated. In the analysis with the first option, the required volume which was about 0.32 ml-1.24 ml showed a very fast change of color. Although the required volume in this test was low, the obtained concentrations were satisfactory (see table

I-1 in appendix II). However, the analysis of this sample was conducted using 0.0001250 M AgNO_3 which there was not any concern about the fast color change during the titration. The obtained results from the analysis 10 ppm cyanide solution are presented in figure 30 and table 27.

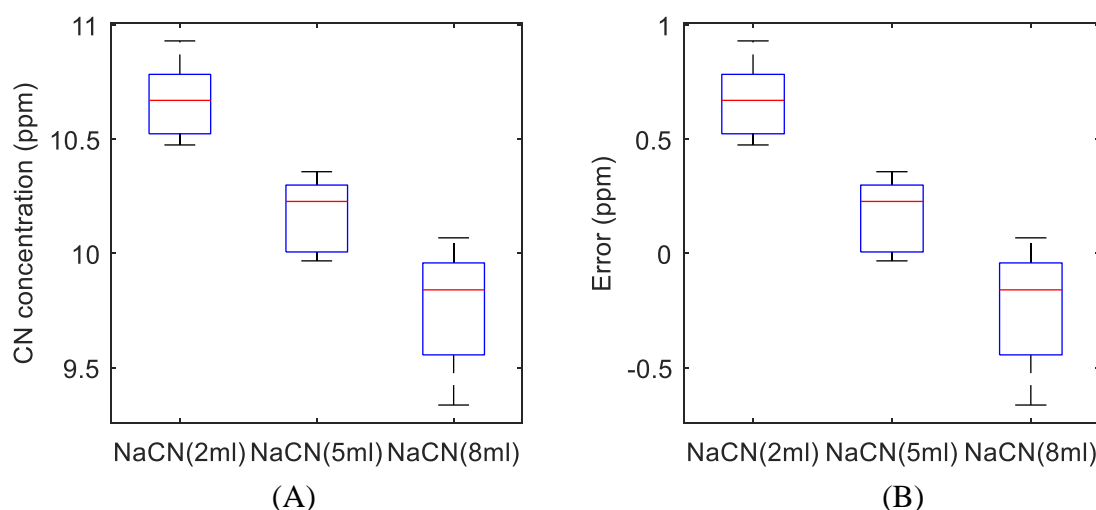


Figure 30. Results from the titration of 10 ppm cyanide solution with 0.0001250 M AgNO_3 : (A) CN concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 27. The average concentrations, standard deviations, average errors, and % errors in the titration of the 10 ppm cyanide solution with 0.0001250 M AgNO_3 as titrant and rhodanine as the indicator.

Sample volume (ml)	Titrant concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	0.0001250	10.66	0.17	0.66	6.62
5	0.0001250	10.16	0.16	0.16	1.62
8	0.0001250	9.75	0.28	-0.24	-2.49

According to table 27, the average of the obtained concentrations in the analysis 5 ml sample volume with this titrant was closer to the expected concentration. Therefore, the 0.0001250 M AgNO_3 as the titrant, rhodanine as the indicator, and 5 ml sample volume could successfully determine approximately 10 ppm free cyanide in this cyanide solution; the error was about 1.62%.

The analysis of 5 ppm cyanide solution was conducted using 0.0001250 M AgNO_3 . The achieved data for this sample is presented in figure 31 and table 28.

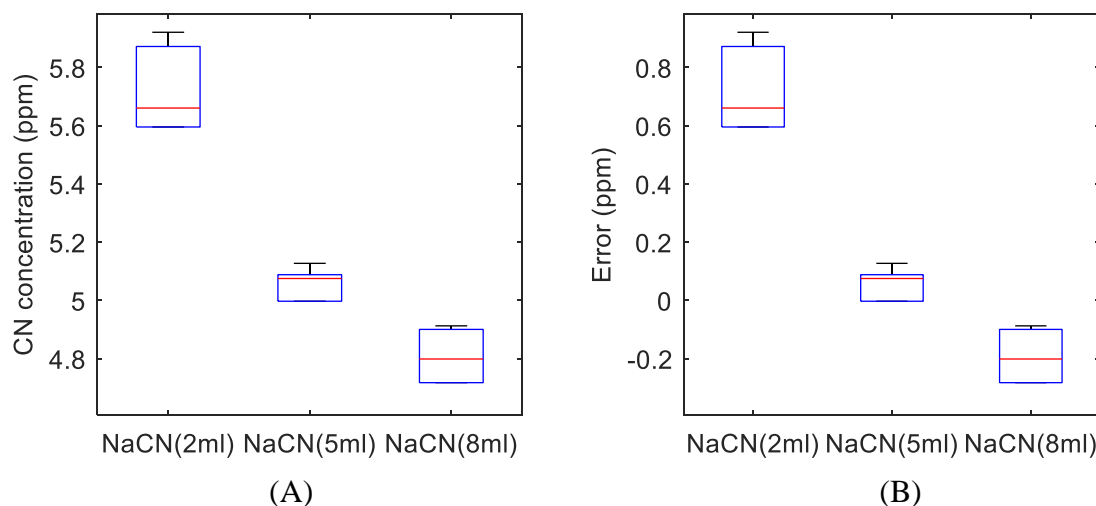


Figure 31. Results from the titration of 5 ppm cyanide solution with 0.0001250 M AgNO_3 : (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 28. The average concentrations, standard deviations, average errors, and % errors in the titration of the 5 ppm cyanide solution with 0.0001250 M AgNO_3 as titrant and rhodanine as the indicator.

Sample volume (ml)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	5.72	0.15	0.72	14.50
5	5.05	0.05	0.05	1.08
8	4.80	0.09	-0.19	-3.84

As can be seen in table 28, the average of the obtained concentrations in the analysis of 2 ml sample volume which is 5.72 ppm was higher than the expected concentration. On the other hand, in the analysis of 8 ml sample volume, the average concentration of about 4.80 ppm was lower than 5 ppm. Therefore, the 0.0001250 M AgNO_3 as the titrant, rhodanine as the indicator, and 5 ml sample volume with the lowest error of about 1.08% were the optimum options for the determination of 5 ppm free cyanide in this solution.

For the determination of free cyanide concentration in 1 ppm cyanide solution, the 0.0001250 M AgNO_3 and 0.0000125 M AgNO_3 were evaluated. In case of using the second

titrant for analysis of 5 ml sample, the required volume was too large ($8.6 \text{ ml} \leq V_{\text{titrant}} \leq 9.28 \text{ ml}$). Hence, this drawback made its application problematic for CN^- identification. Although in the analysis with $0.0001250 \text{ M AgNO}_3$ the required volumes were too small ($0.78 \text{ ml} \leq V_{\text{titrant}} \leq 0.88 \text{ ml}$), this titrant due to the better visual detection was selected. The results of the analysis 1 ppm cyanide solution with $0.000125 \text{ M AgNO}_3$ are presented in figure 32 and table 29. The results of the analysis 1 ppm cyanide solution with $0.0000125 \text{ M AgNO}_3$ are presented in appendix II as table II-2.

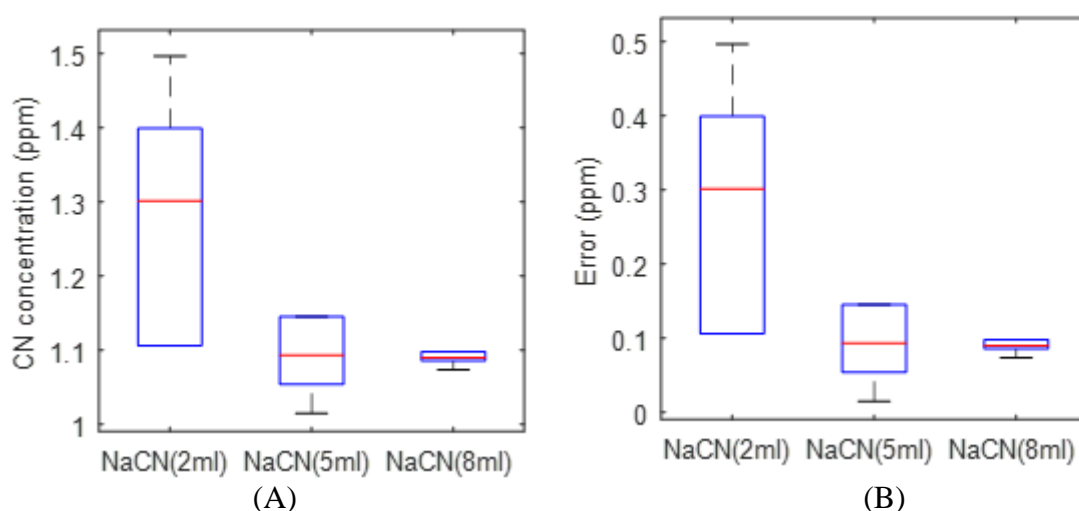


Figure 32. Results from the titration of 1 ppm cyanide solution with $0.0001250 \text{ M AgNO}_3$: (A) CN^- concentrations, and (B) errors. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 29. The average concentrations, standard deviations, average errors, and % errors in the titration of the 1 ppm cyanide solution with $0.0001250 \text{ M AgNO}_3$ as titrant and rhodanine as the indicator.

Sample volume (ml)	Titrant concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	0.0001250	1.27	0.16	0.27	27.5
5	0.0001250	1.09	0.05	0.09	9.3
8	0.0001250	1.09	0.01	0.09	9.3

As can be seen in table 29, the average concentrations in the analysis 5 ml and 8 ml sample volume with this titrant were close to the expected concentration. However, in the analysis 8 ml sample volume, the standard deviation was lower (0.01 ppm). Therefore, the 0.0001250

M $AgNO_3$ as titrant and rhodanine as the indicator can successfully determine free cyanide concentration in either 5 ml or 8 ml sample volume.

7.2.1 The optimum concentrations of titrant

The optimum concentrations of the titrant for the determination of free cyanide concentration in 1 to 100 ppm cyanide solution with rhodanine as the indicator are presented in table 30. Like the first series of experiments, the best sample volume was 5 ml due to the same reasons discussed in section 7.1.1.

Table 30. Samples and their most suitable titrant in the determination of cyanide with rhodanine as the indicator.

Concentration of the sample (ppm)	Samples volumes (ml)	Titrant		
		0.0012500 M $AgNO_3$	0.0001250 M $AgNO_3$	0.0000125 M $AgNO_3$
100	5	✓	-	-
75	5	✓	-	-
50	5	✓	-	-
10	5	×	✓	-
5	5	-	✓	-
1	5	-	✓	×
✓ Minimum error × Unacceptable - Not tested				

7.2.2 The reliability of the indicator

According to the calculated standard deviations and errors, rhodanine is a reliable indicator for the determination of free cyanide concentration in 5-100 ppm cyanide solutions. The calculated values are presented in table 31. As can be seen, the highest error was in the analysis of 1 ppm cyanide solution. This lack of precision can be due to the difficulty in the detection of the color change to mark the end-point, which is shown in figure 33. According to this figure, 1 ppm sample ended up in a yellow color, which provided a low contrast for end-point detection. On the other hand, 10 ppm sample showed a pink color at its end-point, which provided high contrast to the primary color of the solution and consequently easier detection of the end-point. As can be seen in table 24 to table 26, the % of error in the analysis

5 ml sample volume decreased by decreasing the cyanide concentration. However, in table 27 to table 29, this value increased from 1.62% to 9.3% by decreasing the cyanide concentration in the solution.

Table 31. The numerical results achieved from the titration of 5 ml cyanide solutions with AgNO_3 as titrant and rhodanine as the indicator.

Sample concentration(ppm)	Titrant concentration M AgNO_3	Standard deviation (ppm)	Average error (ppm)	Average error (%)
100	0.0012500	0.83	0.09	0.09
75	0.0012500	1.99	-0.56	-0.75
50	0.0012500	1.42	-0.81	-1.62
10	0.0001250	0.16	0.16	1.62
5	0.0001250	0.05	0.05	1.08
1	0.0001250	0.05	0.09	9.30

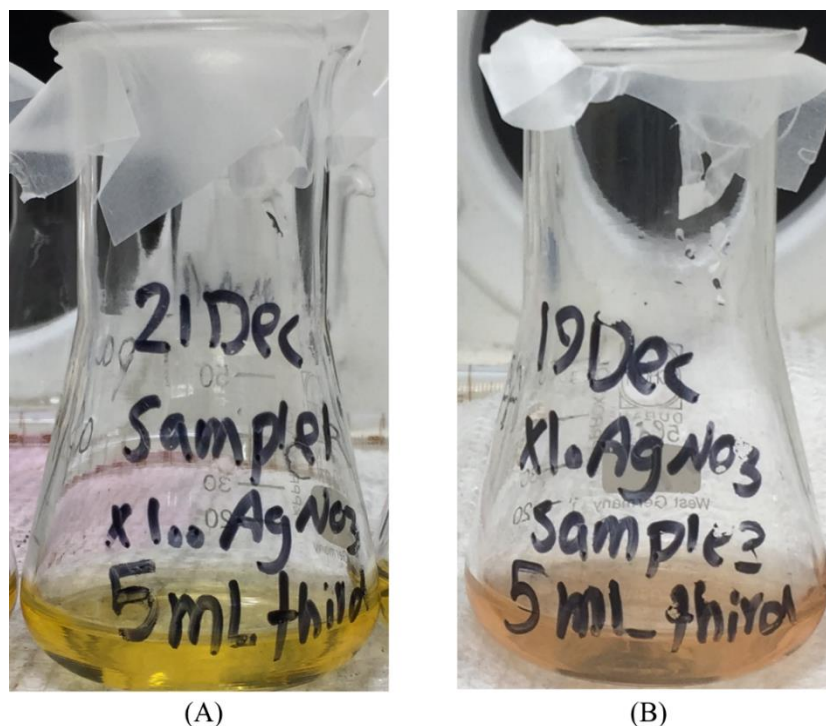


Figure 33. End-points of two different samples (A) 1 ppm CN^- ; (B) 10 ppm CN^- .

7.3 Results and discussion of the third series of experiments

Three samples with the CN^- concentrations value of 100, 10, and 1 ppm were investigated with AgNO_3 as titrant and rhodanine as the indicator. Each sample contained 1000 ppm SO_4^{2-} , 10 ppm NO_3^- , 15 ppm NH_4^+ , and 100 ppm Cl^- . Furthermore, box plots from the data

achieved from these samples with 100, 10, and 1 ppm pure cyanide solutions are compared in figure 34 to figure 36. Finally, the average concentrations, standard deviations, average errors, and % errors in the titrations are presented in table 32 to table 34 at the end of this section.

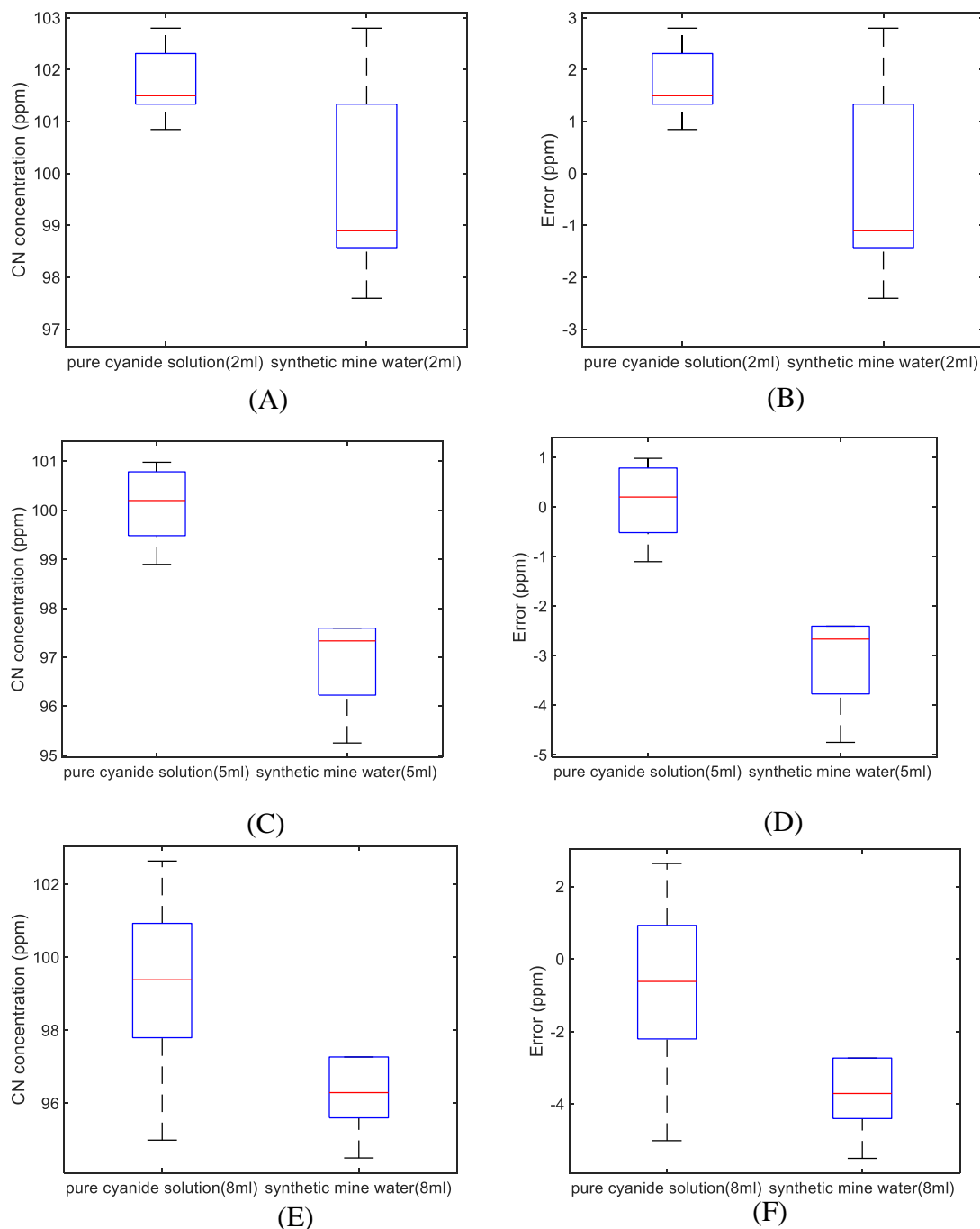


Figure 34. CN^- concentrations and errors from the analysis of 100 ppm cyanide solution and synthetic mine water with 0.0012500 M $AgNO_3$ as titrant and rhodanine as the indicator: (A & B) 2 ml; (C & D) 5 ml; (E & F) 8 ml. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

The analysis of synthetic mine water containing 10 ppm free cyanide was conducted using 0.0001250 M AgNO_3 . The optimum titrant concentration for this sample was selected based on the conducted experiment in section 7.2 for 10 ppm cyanide solution.

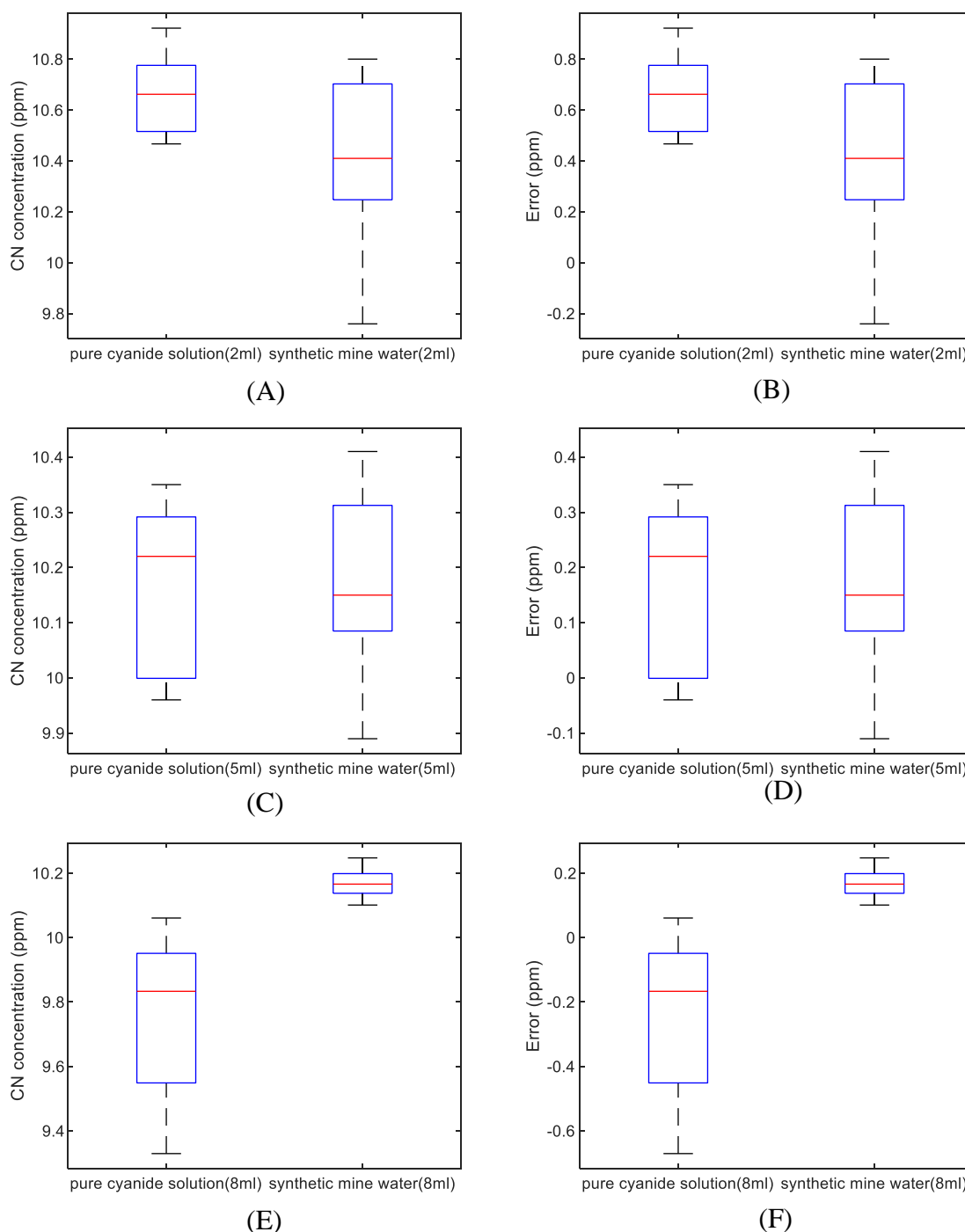


Figure 35. CN^- concentrations and errors from the analysis of 10 ppm cyanide solution and synthetic mine water with 0.0001250 M AgNO_3 as titrant and rhodanine as the indicator: (A & B) 2 ml; (C & D) 5 ml; (E & F) 8 ml. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

The analysis of synthetic mine water containing 1 ppm free cyanide was conducted using 0.0001250 M AgNO_3 . The optimum titrant concentration for this sample was selected based on the conducted experiment in section 7.2 for 1 ppm cyanide solution.

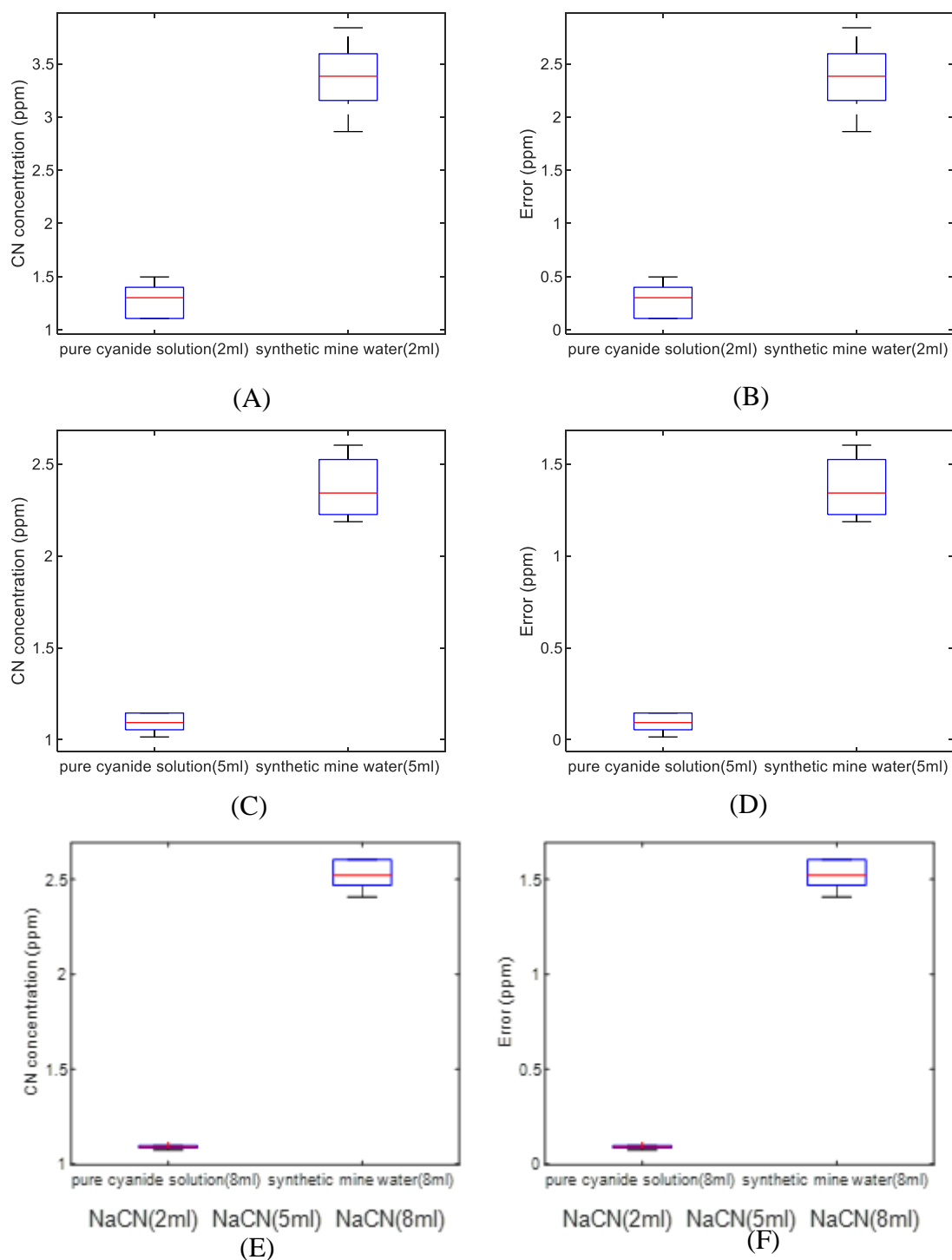


Figure 36. CN^- concentrations and errors from the analysis of 1 ppm cyanide solution and synthetic mine water with 0.0001250 M AgNO_3 as titrant and rhodanine as the indicator: (A & B) 2 ml; (C & D) 5 ml; (E & F) 8 ml. Black lines show the maximum and minimum data, blue box shows upper and lower quartile, and red line the median value.

Table 32. The average concentrations, standard deviations, average errors, and % errors in the titration of synthetic mine water containing 100 ppm cyanide with 0.0012500 M AgNO_3 as titrant and rhodanine as the indicator.

Sample volume (ml)	Titration concentration M AgNO_3	Average of the obtained concentration (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	0.0012500	99.80	2.03	-0.19	-0.19
5	0.0012500	96.86	0.99	-3.13	-3.13
8	0.0012500	96.26	1.14	-3.73	-3.73

Table 33. The average concentrations, standard deviations, average errors, and % errors in the titration of synthetic mine water containing 10 ppm cyanide with 0.0001250 M AgNO_3 as titrant and rhodanine as the indicator.

Sample volume (ml)	Titration concentration M AgNO_3	Average of the obtained concentration (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	0.0001250	10.41	0.40	0.41	4.1
5	0.0001250	10.17	0.19	0.17	1.75
8	0.0001250	10.16	0.05	0.16	1.69

Table 34. The average concentrations, standard deviations, average errors, and % errors in the titration of synthetic mine water containing 1 ppm cyanide with 0.0001250 M AgNO_3 as titrant and rhodanine as the indicator.

Sample volume (ml)	Titration concentration M AgNO_3	Average of the obtained concentration (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
2	0.0001250	3.37	0.35	2.37	237.0
5	0.0001250	2.37	0.17	1.37	137.3
8	0.0001250	2.52	0.08	1.52	152.4

The obtained results showed that rhodanine can be successfully applied for the determination of cyanide concentration in synthetic mine water with 10-100 ppm free cyanide. The presence of 15 ppm NH_4^+ , 10 ppm NO_3^- , 1000 ppm SO_4^{2-} , and 100 ppm Cl^- did not cause significant interference. However, this method was not efficient enough for concentrations as small as 1 ppm. As can be seen in table 35, the error in synthetic mine water containing 1 ppm free cyanide was 137.35% which was really higher in comparison to cyanide solution with 1 ppm free cyanide (9.30%). The possible reason for this very high error can be due to the difficulty in the visual detection (see figure 33) and maybe the presence of other

compounds in the synthetic mine water. The standard deviation, average error, % error in the titration of 5 ml of synthetic mine water and cyanide solution are compared in table 35.

Table 35. The comparison between standard deviations, average errors, and % errors in the titration of 5 ml of synthetic mine water and cyanide solutions with $AgNO_3$ as titrant and rhodanine as the indicator.

Sample concentration (ppm)	Synthetic mine water			Cyanide solution		
	Standard deviation (ppm)	Average error (ppm)	Average error (%)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
100	0.99	-3.13	-3.13	0.83	0.09	0.09
10	0.19	0.17	1.75	0.16	0.16	1.62
1	0.17	1.37	137.35	0.05	0.09	9.30

In conclusion, this study showed that $AgNO_3$ as the titrant and rhodanine as the indicator can determine cyanide in synthetic mine water. In the analysis of synthetic mine water with 100 ppm free cyanide, the average error was -3.13%. In comparison to some similar studies, which considered copper as the interference, this average value was in a more acceptable criterion. As an example, Jimenez-Velasco et.al (2014) studied the determination of free cyanide concentration with $AgNO_3$ as titrant and rhodanine as the indicator. The calculated error in a solution containing 100 ppm cyanide and 61 ppm copper was 121%.

In another study, Breuer et.al (2011) studied the determination of free cyanide concentration with $AgNO_3$ as titrant and rhodanine as the indicator. The calculated error in a solution containing 250 ppm cyanide and 500 ppm copper was 94%. The comparison of these studies with the current one shows that rhodanine is a reliable indicator in the presence of 15 ppm NH_4^+ , 10 ppm NO_3^- , 1000 ppm SO_4^{2-} , and 100 ppm Cl^- . However, in the presence of copper cyanide species, such as $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$ this method is associated with high errors. The reaction of these species with $AgNO_3$ and the consumption of titrant are the main reasons for overestimated results for free cyanide concentration. Therefore, the potentiometric end-point method is the preferable option for the determination of cyanide in solutions with high copper concentration.

8 CONCLUSIONS

Cyanide can be found in the effluents of numerous industries including mining. The toxicity and the concentration control of cyanide during gold and silver extractions necessitate the precise detection and determination of this compound. Hence, the main aim of this research was finding and then comparing experimentally the different available methods for analyzing cyanide. Among different analysis method, silver nitrate titration as the most commonly applied method in gold extraction industry was selected to determine free cyanide concentration in aqueous solutions.

For this purpose, three series of experiments were conducted. In the first series of experiments, $AgNO_3$ as the titrant and KI in the presence of NH_4OH as the indicator were applied. In the second series of the experiments, $AgNO_3$ as the titrant and rhodanine as the indicator was used to determine the free cyanide concentration. In addition, the effect of main interferences including sulfate, nitrate, ammonium, and chloride, on this analysis was studied in the third series of the experiments.

In the first series of the experiments, the cyanide concentration was determined in 6 samples containing 100, 75, 50, 10, 5, 1 ppm free cyanide. The analysis was conducted in 2 ml, 5 ml, and 8 ml sample volume; in addition, each sample was titrated 5 times. 0.010, 0.001, and 0.002 M $AgNO_3$ as the titrant and 10% KI , 10% NH_4OH were prepared as the indicator. The average error which varied from -1.51% to 64.95% showed that this indicator was not reliable enough for free cyanide determination.

In the second series of the experiment, the similar procedure with different titrant concentrations of 0.0012500, 0.0001250, and 0.0000125 M was conducted. The average error which varied from -0.75% to 9.3% showed that the indicator was reliable for the determination of samples with 5 ppm cyanide and higher. Hence, the 0.0012500 M $AgNO_3$ was selected for the analysis of synthetic mine water with 100 ppm free cyanide. In addition, 0.0001250 M $AgNO_3$ was chosen for the analysis of synthetic mine water with 10 ppm and 1 ppm free cyanide.

The last series of experiment, carried out using the optimum titrant and three different samples volume, showed that $AgNO_3$ as the titrant and rhodanine as the indicator could successfully be applied for the free cyanide determination in the samples with 10 ppm cyanide and higher. In addition, the presence of 1000 ppm sulfate, 10 ppm nitrate, 15 ppm ammonium, and 100 ppm chloride did not cause any significant interferences. However, this method was not efficient enough for concentrations as small as 1 ppm. The possible reason for the higher error of about 137.35% could be due to the difficulty in the visual detection and maybe the presence of main interferences in the synthetic mine water.

Further research on the free cyanide determination can be conducted in the presence of other interferences which normally are found in mining effluents. These interferences include $S_2O_3^{2-}$, SCN^- , $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, WAD cyanide, Zn^{+2} , S^{2-} , CNO^- , NO_3^- , and C_2N_2 . The effect of each interference can be studied individually and in the presence of other interferences. Also, the decomposition of these components can be investigated in the simulated environment to mining sites. By knowing the decomposition rate, the over or lower estimated results can be interpreted more scientifically.

Based on the literature review, among different analysis method, the flow injection analysis is a promising method for the determination of free cyanide concentrations in aqueous solutions. In this method, all the associated cyanide in the cyanide complexes are liberated before the test starts. Moreover, the low detection limit of about 0.01-200 ppm can meet the strict emission standards to preserve the human health and the environment.

APPENDICES

Appendix I Results when KI in the presence of NH_4OH was used as the indicator.

Appendix II Results when rhodanine was used as the indicator.

REFERENCES

Alonso-González, O., Jiménez-Velasco, C., Nava-Alonso, F., Alvarado-Hernández, F. & González-Anaya, J. 2017. Free cyanide analysis by silver nitrate titration with sulfide ion as interference. *Mineral Engineering*, 105, Pp. 19-21.

Archer, E. E. 1958. The Argentimetric Titration of Halide and Cyanide Ions with Dithizone as Indicator. *Analyst*, 83, Pp. 571-579.

ASTM D2036-06, 2006. Standard Test Methods for Cyanides in Water, ASTM International, West Conshohocken, PA.

ASTM D6888-04, 2004. Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection, West Conshohocken, PA.

Babut, G. B., Moraru, R. I. & Babut, M. C. 2010. Cyanide Management in Mining: An Integrated Occupational-Environmental Approach. *Annual of the University of Mining and Geology "St. Ivan Rilski"*, 53, Pp. 48-54.

BarbenAnalytical. 2015. Application Note: Cyanide Leach Process- pH. [web document]. Published 2015 [Referred_18.7.2018]. Available: http://www.barbenanalytical.com/files/Gold_Cyanide_AN_RevA.pdf.

Bark, L. S. & Higson, H. G. 1963. A Review of the Methods Available for the Detection and Determination of Small Amounts of Cyanide. *Analyst*, 88: 1051, Pp. 751-760.

Barnes, D. E., Wright, P. J., Graham, S. M. & Jones-Watson, E. A. 2000. Techniques for the Determination of Cyanide in a Process Environment: A Review. *Geostandards Newsletter*, 24: 2, Pp. 183-195.

Bazrafshan, E., Ownagh, K. A. & Mahvi, A. H. 2012. Application of Electrocoagulation Process Using Iron and Aluminum Electrodes for Fluoride Removal from Aqueous Environment. *Journal of Chemistry*, 9: 4, Pp. 2297-2308.

Birmingham City University, 2011. Dot and cross structure of CN^- . [web document]. Published 2011. [Referred 29.7.2018]. Available at: <https://www.thestudentroom.co.uk/showthread.php?t=1640049>

Bojorge Ramírez, N., Salgado, A. M. & Valdman, B. 2009. The Evolution and Developments of Immunosensors for Health and Environmental Monitoring: Problems and Perspectives. *Brazilian Journal of Chemical Engineering*, 26: 2, Pp. 227-249.

Botz, M. M. 2001. Overview of Cyanide Treatment Methods. *Mining Environmental Management*, Pp. 1-30.

Botz, M., Mudder, T. & Akcil, A. 2005. Cyanide Treatment: Physical, Chemical and Biological Processes. In: Adams, M. D, *Advances in Gold Ore Processing*. New York: Elsevier, Pp. 693-697.

Breuer, P. L., Sutcliffe, C. A. & Meakin, R. L. 2011. Cyanide Measurement by Silver Nitrate Titration: Comparison of Rhodanine and Potentiometric End-points. *Hydrometallurgy*, 106: 3, Pp. 135-140.

Burgot, J. L. 2012. Titrimetric Methods Involving a Precipitation. In: Burgot, J. L. *Ionic Equilibria in Analytical Chemistry*. New York: Springer-Verlag, Pp. 700-701.

Cameron, M. 2002. Picric Acid Hazards. [web document]. Published 2002, [Referred 19.7.2018]. Available at: <https://oag.ca.gov/sites/all/files/agweb/pdfs/cci/safety/picric.pdf>

Chaturvedi, S. I. 2013. Electro-Coagulation: A Novel Wastewater Treatment Method. *International Journal of Modern Engineering Research*, 3: 1, Pp. 93-100.

Chemistry102. 2013. Titration. [web document]. Published 2013, [Referred 19.7.2018]. Available at: http://www.webassign.net/question_assets/ncsugenchem102labv1/lab_9/manual.html

Comninellis, C. & Chen, G. 2010. Electrochemistry for the Environment. New York: Springer, Pp. 245-246.

Ribbecca, S. 2014. The Data Visualization Catalogue. [web document]. Published 2014. [Referred 25.9.2018]. Available at: http://www.datavizcatalogue.com/methods/box_plot.html

Dai, X. 2005. The Development of a Flow Injection Analysis Method for the Quantification of Free Cyanide and Copper Cyanide Complexes in Gold Leaching Solutions. Hydrometallurgy, 76: 1-2, Pp. 87-96.

Destanoğlu, O. & Gümüş Yilmaz, G. 2016. Determination of Cyanide, Thiocyanate, Cyanate, Hexavalent Chromium, and Metal Cyanide Complexes in Various Mixtures by Ion Chromatography with Conductivity Detection. Journal of Liquid Chromatography, 39:9, Pp. 465-474.

Donato, D. B., Nichols, O., Possingham, H., Moore, M., Ricci, P. F., Noller, B. N. 2007. A Critical Review of the Effects of Gold Cyanide-bearing Tailings Solutions on Wildlife. Environment International, 33:7, Pp. 974-984.

Eden, G. E., Hampson, B. L. & Wheatland, A. B. 1950. Destruction of Cyanide in Waste Waters by Chlorination, Journal of Chemical Technology and Biotechnology, 69: 8, Pp. 244-249.

Egekeze, J. O. & Oehme, F. W. 2011. Cyanides and Their Toxicity: A Literature Review. Veterinary Quarterly, 2: 2, Pp. 104-114.

Eisler, R. 1991. Cyanide Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review, Washington DC: U.S. Department of the Interior, Fish and Wildlife Service, Pp. 281-284.

EPA. 2010a. Toxicological Review of Hydrogen Cyanide and Cyanide Salts, Washington, D.C.: U.S. Environmental Protection Agency. 91 p.

EPA. 2010b. Method OIA 1677-09: Available Cyanide by Ligand Exchange and Flow Injection Analysis (FIA), Washington, D.C.: U.S. Environmental Protection Agency. 2 p.

Eyvaz, M. 2016. Treatment of Brewery Wastewater with Electrocoagulation: Improving the Process Performance by Using Alternating Pulse Current. *International Journal of Electrochemistry Science*, 111, Pp. 4988-5008.

Garcia-Segura, S., Eiband, M. M. S., De Melo, J. V. & Martínez -Huitle, C. 2017. Electrocoagulation and Advanced Electrocoagulation Processes: A General Review about the Fundamentals, Emerging Applications and Its Association with other Technologies, *Journal of Electroanalytical Chemistry*, 801, Pp. 267-299.

Gary, L., Miessler, P. J., Fischer, D. & Tarr, A. 2014. *Inorganic Chemistry*, New York: Pearson. 169 p.

Ghous, T. 1999. Flow Injection Analysis (FIA). *Journal of the Chemical Society of Pakistan*, 21: 4, Pp. 375-381.

Giuriati, C., Cavalli, S., Gorni, A., Badocco, D., Pastore, P. 2004. Ion Chromatographic Determination of Sulfide and Cyanide in Real Matrices by Using Pulsed Amperometric Detection on a Silver Electrode. *Journal of Chromatography A*, 1023: 1, Pp. 105-112.

Geological Survey of Finland. 2009. Vapaan Syanidipitoisuuden Määrtys Titraamalla Hopeanitaatilla. Published 2009. [Referred 31.7.2018].

Hansen, E. H. & Wang, J. 2004. The Three Generations of Flow Injection Analysis. *Analytical Letters*, 37: 3, Pp. 345-359.

Harvey, D. 2000. *Modern Analytical Chemistry*. New York: McGraw-Hill. 274 p.

Jaszczak, E., Polkowska, Ż., Narkowicz, S. & Namieśnik, J. 2017. Cyanides in the Environment—analysis—problems and Challenges. *Environmental Science and Pollution Research*, 24: 19, Pp. 15929-15948.

Jenny, R., Botz, M. M., Dimitriadis, D., Polglase, T., Phillips, W. 2001. Processes for the Regeneration of Cyanide from Thiocyanate. *Minerals and Metallurgical Processing*, 18: 126-132, Pp. 126-132.

Jimenez-Velasco, C., Nava-Alonso, F., Uribe-Salas, A. & Alonso-Gonzalez, O. 2014. Thermodynamic Analysis of Free Cyanide Determination by Silver Nitrate Titration in Copper Bearing Solutions. *Canadian Metallurgical Quarterly*, 53: 2, Pp. 207-212.

Kem Kyoto Electronics Manufacturing CO., LTD. 2018. Kem Application Note: Free cyanide in Silver plating solution Titrator [web document]. Published 2018. [Referred 22.7.2018]. Available at: <http://www.kyoto-kem.com/en/pdf/industry/IronandSteel/ETIN-01002.pdf>

Kitis, M., Akcil, A. & Karakaya, E. Y. N. O. 2005. Destruction of Cyanide by Hydrogen Peroxide in Tailings Slurries from Low Bearing Sulphidic Gold Ores. *Journal of Minerals Engineering*, 18: 3, Pp. 353-362.

Koby, M., Demirbas, E., Ozyonar, F., Sirtbas, G., Gengec, E. 2017. Treatments of Alkaline Non-cyanide, Alkaline Cyanide and Acidic Zinc Electroplating Wastewaters by Electrocoagulation. *Process Safety and Environmental Protection*, 105, Pp. 373-385.

Koby, M., Demirbas, E., Parlak, N. U. & Yigit, S. 2010. Treatment of Cadmium and Nickel Electroplating Rinse Water by Electrocoagulation. *Environmental Technology*, 31: 13, Pp. 1471-1481.

Kuyucak, N. & Akcil, A. 2013. Cyanide and Removal Options from Effluents in Gold Mining and Metallurgical Processes. *Minerals Engineering*, Pp. 13-29.

Lindler, E. & Pendley, B. D. 2013. A Tutorial on the Application of Ion-selective Electrode Potentiometry: An Analytical Method with Unique Qualities, Unexplored Opportunities and Potential Pitfalls. *Analytica Chimica Acta*, 762, Pp. 1-13.

Lipták, B. & Venczel, K. 2016. *Analysis and Analyzers*, New York: CRC Press. 271 p.

Lister, M. W. 1955. Some Observations on Cyanic Acid and Cyanates. *Canadian Journal of Chemistry*, 33:2, Pp. 426-440.

Logsdon, M. J., Hagestein, K. & Mudder, T. 1999. *The Management of Cyanide in Gold Extraction*. Ottawa: International Council on Metals and the Environment, Pp. 20-27.

Lottermoser, B. 2010. *Mine Wastes*, 3rd ed. Berlin: Springer-Verlag, Pp. 243-244.

Marriaga-Cabrales, N. & Machuca-Martínez, F., 2014. Fundamentals of electrocoagulation. In: Peralta-Hernández, J. M., Rodrigo-Rodrigo, M. A. & Martínez-Huitle, C. A. In: *Evaluation of Electrochemical Reactors as a New Way to Environmental Protection*, Kerala: Research Signpost, Pp. 1-16.

Mendham, 2006. *Vogels Textbook of Quantitative Chemical Analysis*. 6th ed. New York: Pearson Education. 358 p.

Milosavljevic, E. 2013. Measurement of Weak and Dissociable (WAD) Cyanide with a Modified Potentiometric Titration. *Minerals & metallurgical Processing*, 30: 4, Pp. 191-204.

Moran, R. E. 1999. Cyanide in Mining- Some Observations on the Chemistry, Toxicity and Analysis of Mining-Related Waters, *Central Asia Ecology*, Pp. 1-10.

Moussa, D. T., El-Naas, M. H., Nasser, M. & Al-Marri, M. J. 2017. A Comprehensive Review of Electrocoagulation for Water Treatment: Potentials and Challenges. *Journal of Environmental Management*, 186, Pp. 24-41.

Moussavi, G., Majidi, F. & Farzadkia, M. 2011. The influence of Operational Parameters on Elimination of Cyanide from Wastewater Using the Electrocoagulation Process. *Desalination*, 280: 1-3, Pp. 127-133.

Mudder, T. I., Botz, M. & Smith, A. 2001. *Chemistry and Treatment of Cyanidation Wastes*, London: Mining Journal Books. Pp. 1-44.

Nollet, L. M. L. & De Gelder, L. S. P. 2007. Chromatographic (Electrophoretic) Technique. In: *Handbook of Water Analysis*. 2nd ed. New York: CRC Press, Pp. 540-543.

Norman, D. K. & Raforth, R. L. 1994. *Cyanide Heap Leaching*, Washington DC: Washington State Department of Natural Recourses. 3 p.

OCEANAGOLD. 2015. The Mining Process. [web document]. Published 2015. [Referred 18.7.2018]. Available at: <http://www.waihigold.co.nz/mining/the-mining-process/>

Parga, J. R., Shukla, S. S. & Carrillo-Pedroza, F. R. 2003. Destruction of Cyanide Waste Solutions Using Chlorine Dioxide, Ozone and Titania. *Waste Management*, 23:2, Pp. 183-191.

Pohlandt, A. F., Jones, C. & Lee, E. A. 1983. A Critical Evaluation of Methods Applicable to the Determination of Cyanides. *Journal of the Southern African Institute of Mining and Metallurgy*, 83: 1, Pp. 11-19.

Ryan, J. A. & Culshaw, G. W. 1944. The Use of p -Dimethylaminobenzylidene Rhodanine as an indicator for the volumetric determination of cyanides. *Analyst*, 69: 825, Pp. 370-371.

Robards, K., Haddad, P. R. & Jackson, P. E. 1994. *Principles and Practice of Modern Chromatographic Methods*. San Diego: Elsevier. Pp. 265-266.

Sarwar, M., Rashid, A. & Fatima, B. 1973. Micro-determination of Cyanide, *Analytical Letters*, 6: 8, Pp. 755-759.

Sentruk, E. 2013. The Treatment of Zinc-cyanide Electroplating Rinse Water Using an Electrocoagulation Process. *Water Science and Technology*, 68: 10, Pp. 2220-2227.

Siddiqui, M. R., Alothman, Z. A. & Rahman, N. 2017. Analytical techniques in Pharmaceutical Analysis: A review. *Arabian Journal of Chemistry*, 10, Pp. 1409-1421.

Simeonova, F. P. & Fishbein, L. 2004. Hydrogen Cyanide and Cyanides. Geneva: World Health Organization. Pp. 4-10.

Simovic, L. 1984. Kinetics of Natural Degradation of Cyanide from Gold Mill Effluents (Doctoral Thesis). Hamilton: McMaster University. Pp. 33-38.

Singh, H. B. & Wasi, N. M. M. C. 1986. Detection and Determination of Cyanide-A Review. *International Journal of Environmental Analytical Chemistry*, 26:2, Pp. 115-136.

Sulistyarti, H., Cardwell, T. J., De Castro, M. L. & Kolev, S. D. 1999. On-line Determination of Cyanide in the Presence of Sulfide by Flow Injection with Pervaporation. *Analytica Chimica Acta*, 390: 1-3, Pp. 133-139.

Sulistyarti, H. & Kolev, S. 2013. Online Ligand Exchange in the Determination of Weak Acid Dissociable Cyanide by Gas Diffusion-flow injection analysis. *Microchemical Journal*, 111, Pp. 103-107.

Surleva, A., Gradinaru, R. & Drochioiu, G. 2012. Cyanide Poisoning: from Physiology to Forensic Analytical Chemistry. *International Journal of Crime Investigation*, 2, Pp. 79-101.

Taylor, J. 2006. Toxicological Profile for Cyanide, New York: US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Pp. 146-147.

Vepsäläinen, M., Pulliainen, M. & Sillanpää, M. 2012. Effect of Electrochemical Cell Structure on Natural Organic Matter (NOM) Removal from Surface Water through Electrocoagulation (EC). *Separation and Purification Technology*, 99, Pp. 20-27.

Wang, J., 2006. Analytical Electrochemistry. New York: John Wiley & Sons, Pp. 165-166.

Woffenden, M., Noller, B., Noonan, K., Breuer, P., Cooper, P., Donato, D. 2008. Cyanide Management: Leading Practice Sustainable Development Program for the Mining Industry. 1st ed. Canberra: Dept. of Industry, Tourism and Resources. Pp. 88-89.

Young, C. A., Taylor, P. R., Anderson, C. G. & Choi, Y. 2008. Hydrometallurgy 2008: Proceedings of the Sixth International Symposium. 6th ed. Phoenix: Society of Mining, Metallurgy, and Exploration, Inc. Pp. 731-735.

Table I-1. The average concentrations, standard deviations, average errors, and % errors in the titration of the 10 ppm cyanide solution with 0.001 M and 0.010 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator.

Sample volume (ml)	Titrant concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
5	0.010	19.76	-	9.76	97.6
5	0.001	1.65	-	-8.35	-83.5

Table I-2. The average concentrations, standard deviations, average errors, and % errors in the titration of the 5 ppm cyanide solution with 0.001 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator.

Sample volume (ml)	Titrant concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
5	0.001	1.44	-	-3.56	-71.16

Table I-3. The average concentrations, standard deviations, average errors, and % errors in the titration of the 1 ppm cyanide solution with 0.002 M AgNO_3 as titrant and KI in the presence of NH_4OH as the indicator.

Sample volume (ml)	Titrant concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
5	0.002	2.92	-	1.92	192

Table II.1. The average concentrations, standard deviations, average errors, and % errors in the titration of the 10 ppm cyanide solution with 0.0012500 M AgNO_3 as titrant and rhodanine as indicator.

Sample volume (ml)	Titration concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
5	0.0012500	10.30	0.23	0.3	3.06

Table II.2. The average concentrations, standard deviations, average errors, and % errors in the titration of the 1 ppm cyanide solution with 0.0000125 M AgNO_3 as titrant and rhodanine as indicator.

Sample volume (ml)	Titration concentration (M)	Average of the obtained concentrations (ppm)	Standard deviation (ppm)	Average error (ppm)	Average error (%)
5	0.0000125	1.15	0.03	0.15	15.70