The development of an online amperometric technique to measure free and WAD cyanide in gold plant leach liquors and effluent streams

By

Wendy A M van der Merwe

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of Cape Town, in fulfilment of the requirements for the Degree Master of Engineering by Research

Johannesburg, 2012

DECLARATION

I declare that this is my own work, save for that which is acknowledged. It is being submitted for the degree of Master of Engineering at University of Cape Town. It has not been submitted before for any degree or examination in any other University.

_____

2nd Day of December 2012

DEDICATION

I dedicate this work to my parents, Christopher Elliott and the late Jean Elliott.

To my mom, who passed away very suddenly during the course of this work:

You will always be remembered for your selfless heart and rich generosity.

I will be forever grateful to you for sacrificing your career to give of yourself to me.

To my dad who patiently answered 'all my questions' growing up and thrust me into a science degree.

Thank you both for believing in my education and encouraging my affinity for science.

ACKNOWLEDGEMENTS

The nature of this project has required the involvement of a team of scientists, engineers and technicians. Since the projects' inception in 2004, my personal responsibility, as the only scientist in the group, has been the development and refinement of the cyanide measurement principle.

I would like to thank Mr P. Lotz and Dr I Barker who were my main technical supervisors during this project, providing cyanide chemistry and electronics knowledge respectively. Also thanks to Mr H Smit, my current immediate supervisor at Mintek and Dr J Petersen, my supervisor at UCT.

Thanks to members of the Instruments group who are involved in Cynoprobe installations all over the world and who assisted me in obtaining plant data; Mr B. Groeneveld, Mr D. van der Spuy, Mr V. Arjun, Mr W. Ahmed, Mr A. Motlhake and Mr R. Mbavhalelo.

For assistance with reference materials and sample analyses, thanks to colleagues in the Cyanide Centre, in particular Mrs S. Janse van Rensburg and Mr P Wright for historical data and cyanide analysis by the SKALAR Segmented Flow Injection instrument.

Thanks to my manager, Mr P. Brereton-Stiles for the financial support to write up this thesis on the work I have been involved in over the years.

Thanks to Anglogold Ashanti, Newmont, Goldfields and Evolution Mining for permission to publish plant data with concealed identity.

SYNOPSIS

Although the cyanidation process for gold extraction has been the topic of much controversy due the highly toxic nature of cyanide and the occurrence of environmental incidents over the years, it is still the lixiviant of choice for gold extraction, as there is no known alternative that can match its overall efficacy and efficiency. However, its continued application is dependent on the demonstration of proper management and the adherence to environmental guidelines, controls and regulatory limits. This can only be achieved if cyanide is frequently measured, controlled and if necessary, destroyed. This includes both free (CN^- ,$HCN_{(aq)}$) and Weak Acid Dissociable (WAD) cyanide which is liberated from associated metals at a moderate pH of 4.5-6. The online measurement of free and WAD cyanide facilitates the optimisation of cyanide addition and destruction control and provides monitoring data required by regulatory bodies.

In 2004, Mintek recognised the gold mining industry's need for an online free and WAD cyanide measurement device and went about extending the existing free cyanide analyser, the Cynoprobe to include WAD cyanide measurement. The WAD cyanide analysis technique was to be based on ligand exchange, which required the selection of an appropriate reagent, with amperometric finish. Thereafter, the technique was validated in the laboratory to include the capabilities of the prototype instrument in terms of accuracy and precision (0.5-100 ppm WAD CN). Various local trials were conducted in order to validate the measurement and the robustness of the instrument in an industrial environment. Successful trials (<10% error with respect to laboratory analysis) led to international application and exposure to complex ore types and process solutions. In order to investigate and resolve interferences from base metals and sulphur species associated with refractory ore types, laboratory test work and development continued simultaneously to commercial implementation. The compatibility of the Cynoprobe's free and WAD cyanide measurement with commercialised destruction oxidants such as sodium meta-bisulphite, hydrogen peroxide and peroxymonosulphuric acid was also investigated and validated.

Over the years, global implementation has led to the generation of free and WAD cyanide concentration data, showing the Cynoprobe's accuracy compared to other techniques. The WAD cyanide measurement was validated against laboratory techniques; micro-distillation with colorimetric finish and gas diffusion ligand exchange with amperometric finish. For WAD cyanide concentrations ranging from 5 to 155 ppm, a percentage error of <10% was

achieved across a variety of ore types, ranging from simple oxides to sulphur and copper rich ores. Online WAD cyanide analysis has also facilitated and monitored cyanide destruction control with the Caro's acid and biological destruction processes, respectively. Finally, environmental discharge monitoring of WAD cyanide concentrations as low as 0.3 ppm has proved invaluable for regulatory compliance at a plant in Africa that has potential for severe environmental and social impact.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
CDTA	Cyclohexylenedi nitrilo-tetraacetic acid
CIP	Carbon In Pulp
DC	Direct Current
DEHPA	Di(ethylhexyl)phosphoric acid
DETA	Diethylenetriamine
DIN	Deutsches Institut für Normung
DL	Detection Limit
DTPA	Diethylenetriaminepenta-acetic acid
DOTA	1,4,7,10-tetraazacyclododecane-N,N',N'',N''-tetraacetic acid
EDA	Ethylenediamine
EDTA	Ethylenediamine tetraacetic acid
EPA	Environmental Protection Agency
FIA	Flow Injection Analysis
FS	Flow Solution
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICME	International Council on Metals and the Environment
ICMI	International Cyanide Management Institute
ICP	Inductively Coupled Plasma
CN-ISE	Cyanide Ion Selective Electrode
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
LDL	Lower Detection Limit
LEX	Ligand Exchange
LoB	Limit of Blank
LoD	Limit of Detection
LoQ	Limit of Quantification
LQL	Lower Quantification Limit
OHP	Outer Helmholtz Plane
OIA	Office of International Activities
PEHA	Pentaethylenehexamine
PLC	Programmable Logic Controller
POX	Pressure Oxidation
PVC	Polyvinyl chloride
RSD	Relative Standard Deviation
SAD	Strong Acid Dissociable
SANS	South African National Standard
SCADA	Supervisory Control and Data Acquisition
SFIA	Segmented Flow Injection Analysis
TEEDA	Tetraethylethylenediamine
TETA	Triethylenetetramine
TEPA	Tetraethylenepentamine
TMEDA	Tetramethylethylenediamine
TDS	Total Dissolved Salts
UQL	Upper Quantification Limit

UNEP	United Nations Environment Programme
US-EPA	United States Environmental Protection Agency
UV	Ulta-violet
WAD	Weak Acid Dissociable
XRF	X-ray fluorescence

CHAPTER ONE

Introduction

The global gold production has been about 2 500 tons per annum since the year 2000 (Chaize, 2011). More than 90% of the gold mined annually is extracted using cyanide (Yarar, 2002). Cyanide is clearly the lixiviant of choice for gold leaching, for both technical and economic reasons. It is still the most effective chemical known for the extraction of silver and gold from rock and cyanide is a common industrial chemical that is readily available at a reasonably low cost.

However, the cyanidation process has been a topic of controversy due to the highly toxic nature of cyanide and the occurrence of environmental disasters in the last two decades. The most infamous disasters have killed few people but have had devastating effects on birds, aquatic and animal life. As a result, local and international authorities introduced stricter regulations to prevent the potential inadvertent release of cyanide into the environment. In May 2000, the "International Cyanide Management Code for the Manufacture, Transport and Use of Cyanide in the Production of Gold" was formed in order to improve the management of cyanide at gold mines. Some American states such as Montana, Colorado and Wisconsin and countries such as Argentina, Turkey, Hungary, and the Czech Republic have gone so far as to ban or partially ban the use of cyanide for mining (Rainforest Information Centre, 2005; Budapest Times, 2010). Although the use of cyanide is considered a risky activity, many argue that its prohibition is extreme (Rodriguez and Macias, 2009, Mudder, 2007 and International Mining, 2010). Environmental spills have all been the result of cyanide mismanagement, in many cases due to the non-existence of controls. According to reputable environmental and cyanide experts such as Logsdon, Hagelstein and Mudder (1999), there is no reason why cyanide should not be used for gold and silver extraction, if it is properly managed and controlled.

The safe use of cyanide by gold mining companies is imperative if the cyanidation process is to continue as the method of choice for gold extraction. In order to prevent surface and ground water contamination, cyanide should be monitored, controlled, recycled and if necessary, destroyed.

For economical reasons, free cyanide has been measured in leach tanks, typically only as the cyanide anion, since the invention of the MacArthur-Forrest Process in 1887. However, in the last two decades the measurement of Weak Acid Dissociable (WAD) cyanide has become necessary

due to environmental concern. WAD cyanide refers to the cyanide bound to metals that is released as toxic free cyanide with a drop in pH to 4.5-6. Incidences such as the North Parkes incident which occurred in Australia in 1995 highlighted the importance of the WAD cyanide measurement. A mineralogy change to copper rich ore caused the WAD cyanide concentration in the tailings dam to increase to 350 ppm, killing approximately 2700 birds, however because the mine was only measuring free cyanide these high WAD cyanide levels were not detected. The occurrence of other environmental disasters resulted in the development of the “International Cyanide Management Code” in the year 2000 which specifies the online measurement of WAD cyanide. Gold mining companies who become signatories to the Code are required to measure WAD cyanide online, and destroy cyanide in excess of the applicable limits.

A few years ago, Mintek recognised the gold mining industry’s need for an online free and WAD cyanide measurement device that could be used for cyanide addition and destruction control as well as monitoring environmental compliance. At this time, there was no online instrument available commercially, which was capable of measuring both free and WAD cyanide. A project was therefore initiated to extend Mintek’s free cyanide analyser, the Cynoprobe, to measure WAD cyanide. The goal of the initial stages of development was to find a WAD cyanide analysis technique that could be combined with free cyanide measurement by amperometry, and explore its feasibility to generate accurate measurements for the analysis of metal cyanide standards in the laboratory, as well as for actual gold leach liquors and effluents under industrial plant conditions. Ultimately, the instrument would be required to be suitable for environmental monitoring and destruction control to assist gold plants in obtaining and maintaining regulatory compliance. The measurable WAD cyanide concentration range should therefore include the International Cyanide Management Code limits of 0.5 and 50 ppm for effluent and tailing storage facilities. Since gold plants exceeding the applicable concentration limits are required to implement cyanide destruction, it also had to be compatible with the most common oxidants.

The project was assigned to the author to work under the supervision of Mr Peter Lotz (International Cyanide Management Institute Technical Expert Auditor) and conduct all experiments necessary to develop and validate a WAD cyanide measurement technique applicable to simple and complex ores. It excluded the design of the hardware and software which required the expertise of an instrument technician and electrical engineer.

CHAPTER TWO

Literature review

2.0 CYANIDE SPECIATION DURING CYANIDATION

Knowledge of the chemical behaviour and stability of the cyanide ion in aqueous gold leach solutions is of importance in terms of measurement, control and detoxification.

Cyanide exists in many forms in gold leach solution. When cyanide is added to an ore pulp containing gold and agitated with air for 18-24 hours, cyanide may either remain unreacted as free cyanide or form complex anions such as cyanate (CNO^-), thiocyanate (SCN^-) and metal cyanide complexes.

2.1 FREE CYANIDE AQUEOUS CHEMISTRY

Unreacted cyanide ions hydrolyse in water to form hydrogen cyanide and hydroxyl ions, according to Equation 2.1.

Equation 2.1 Hydrolysis of cyanide

$$CN^- + H_2O \rightleftharpoons HCN_{(aq)} + OH^-$$

Hydrogen cyanide is a weak acid and its dissociation in water is described by Equation 2.2.

Equation 2.2 Dissociation of cyanide in water

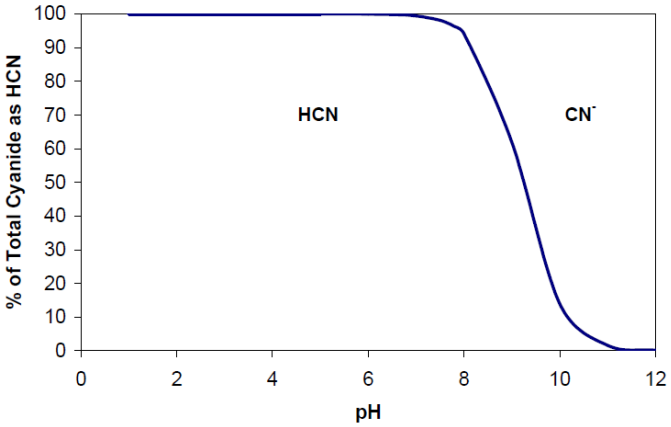
$$HCN_{(aq)} \rightleftharpoons H^+ + CN^- \quad (a)$$

$$K_a = \frac{[H^+][CN^-]}{[HCN]},\ pK_a = 9.31 \text{ at } 25^oC \quad (b)$$

The pH dependence of this dissociation reaction at equilibrium is shown in Figure 2.1. At a pH value equal to the pK_a value, half of the total cyanide exists as hydrogen cyanide and half as free cyanide ions. At a pH less than 7, cyanide exists entirely as $HCN_{(aq)}$ and at a pH greater than 11 it exists as

CN^-. Cyanide leaching systems are operated at a pH typically above 10 but less than 12 so as to minimize cyanide loss by volatisation of $HCN_{(aq)}$ and avoid adversely affecting the mechanism of cyanidation, respectively (Marsden and House, 2006 and Lorösch, 2001). Typically, the amount of cyanide volatilised in an agitation leach plant during the leach is below 5% of the total cyanide added (Lorösch, 2001).

Figure 2.1 Hydrogen cyanide dissociation curve at 25ºC



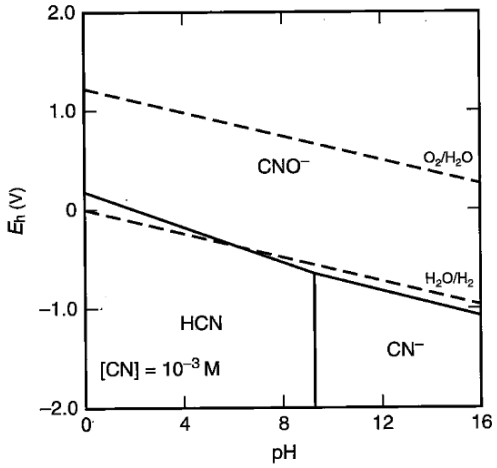
Taken from Amira, 1977.

The potential-pH diagram for the CN-H_2O system at 25ºC is shown in Figure 2.2. At low solution potentials, $HCN_{(aq)}$ and CN^- are the predominant species in solution, depending on the pH. At higher potentials, and especially in the domain of water stability, CNO^- becomes the only stable species. Therefore, according to thermodynamics, cyanide should be spontaneously oxidised to cyanate in aqueous solution at room temperature, according to Equation 2.3. However, because the kinetics of this reaction is extremely slow in the absence of any catalyst it is only formed in concentrations typically <10 ppm or <1% of the applied NaCN (Lorösch, 2001) and cyanidation is economical as a large-scale hydrometallurgical process for gold extraction.

Equation 2.3 Oxidation of cyanide

$$2\ CN^- + O_2 \rightleftharpoons 2\ CNO^-$$

Figure 2.2 Potential-pH diagram for the CN-H_2O system at 25 ºC



Greene, 1996 taken from Marsden and House, 2006

2.1.1 Metal cyanide species

2.1.1.1 The chemistry of gold cyanide

The principal reaction of gold extraction by cyanidation is known as Elsner's equation, according to Equation 2.4.

Equation 2.4 Elsner's equation

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

Cyclic voltammetry reveals that the mechanism of the anodic reaction proceeds via the adsorption of the intermediary species, AuCN which temporarily passivates the gold surface before free cyanide dissolves the adsorbed species to form $[Au(CN)_2]^-$, according to Equation 2.5. In practice, gold passivation is disrupted by the presence of heavy metal ions such as lead and mercury, even at low cyanide concentrations (Marsden and House, 2006).

Equation 2.5 Anodic dissolution of gold

$$Au + CN^- \rightleftharpoons AuCN_{(ads)} + e^- \quad (a)$$
$$AuCN_{(ads)} + CN^- \rightleftharpoons Au(CN)_2^- \ ;\ E^o = 0.61\ V \quad (b)$$

The accompanying cathodic reduction of oxygen may proceed by the formation of either hydroxide

ions (Equation 2.6) or principally by hydrogen peroxide which may be further reduced to hydroxyl ions or decompose to oxygen (Equation 2.7 (a), (b) and (c)) (Marsden and House, 2006).

Equation 2.6 Cathodic reduction of oxygen by the formation of hydroxide ions

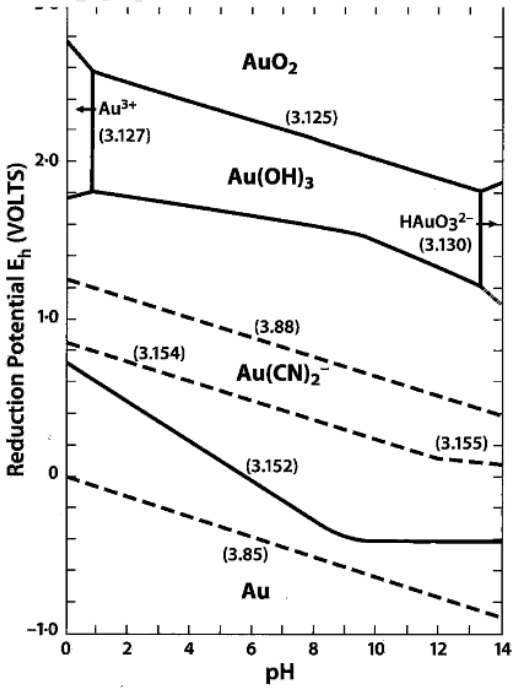
$$O_2 + 2\ H_2O + 4\ e^- \rightleftharpoons 4\ OH^-;\ E^o = 0.401\ V$$

Equation 2.7 Cathodic reduction of oxygen by the formation of hydrogen peroxide

$$O_2 + 2\ H^+ + 2\ e^- = H_2O_2;\ E^o = 0.682\ V \quad (a)$$
$$H_2O_2 + 2\ e^- = 2\ OH^-;\ E^o = 0.88\ V \quad (b)$$
$$2\ H_2O_2 \rightleftharpoons O_2 + 2\ H_2O \quad (c)$$

The potential-pH diagram for Au-CN-H_2O system shown in Figure 2.3 indicates that $[Au(CN)_2]^-$ is the predominant species in almost the total stability domain of water from pH 0-14. The Au(III) cyanide complex, $[Au(CN)_4]^-$ also forms during gold dissolution in cyanide, but is less stable than the Au(I) complex by 0.5 V (Marsden and House, 2006). The diagram indicates that the reduction of oxygen to water can be coupled to anodic gold dissolution, which occurs spontaneously in the presence of cyanide.

Figure 2.3 Potential-pH diagram for the Au-CN-H_2O system at 25ºC



Concentration of all soluble gold species = 10^{-4} mol/L, $[CN^-]_{total}=10^{-3}$ mol/L. Finkelstein, 1972 taken from Lorösch, 2001.

The aurocyanide ion is highly stable, with a stability constant of log β_2 = 39.3 (Sillen and Martell, 1970). Although the affinity of cyanide for gold is such that it is extracted preferentially, cyanide will also form complexes with other metals from the ore, such as zinc, cadmium, lead, copper, nickel, silver, iron, cobalt, platinum and palladium. The presence of empty anti-bonding orbitals in the cyanide ion promote the formation of strong bonds with transition metal ions so that a wide variety of dissolved metal cyanide complexes and soluble mineral decomposition products may be found in the slurry of complex ore types. According to Lorösch (2001), often <1% of cyanide added is consumed for gold dissolution; the rest is involved in other reactions.

2.1.1.2 The chemistry of silver cyanide

Silver is known to occur in substantial quantities in association with gold. Metallic silver dissolves anodically in alkaline cyanide solution in a similar way to gold, according to Equation 2.8. However, the cathodic reaction proceeds only by the four-electron mechanism with direct reduction of oxygen to hydroxyl ions as shown in Equation 2.6 (Lorösch, 2001).

Equation 2.8 Anodic dissolution of silver

$$Ag + 2\ CN^- \rightleftharpoons Ag(CN)_2^- + e^-, \quad E^o = -0.31\ V$$

Silver also often occurs as the sulphide mineral argentite, Ag_2S which reacts with cyanide according to Equation 2.9 (Lorösch, 2001), but the dissolution is slow and reversible and only proceeds at high cyanide concentrations of >0.2% (0.04 mol/L) and if sulphide is removed by simultaneous oxidation to thiosulphate. The complete dissolution of argentite cannot be obtained in the usual retention time of a cyanidation plant.

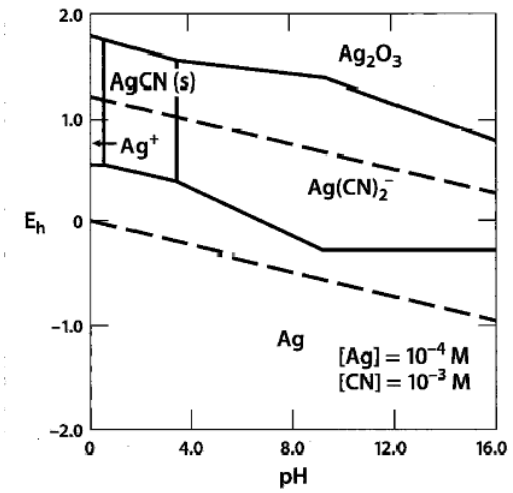
Equation 2.9 Reaction of argentite with cyanide

$$Ag_2S + 4\ CN^- \rightleftharpoons 2\ Ag(CN)_2^- + S^{2-}$$

The potential-pH diagram of the Ag-CN-H_2O system shows the domain of predominant stability of $[Ag(CN)_2]^-$ in practically the entire pH range, but only at elevated potentials (refer to Figure 2.4). Thermodynamically, this confirms that silver will dissolve to form $[Ag(CN)_2]^-$ under the alkaline conditions of gold leaching with cyanide (refer to Figure 2.3).

$AgCN_{(s)}$ forms at low cyanide concentrations such as 10^{-3} M and 10^{-4} M that are well below optimum concentrations for gold extraction (see Figure 2.4). At very high cyanide concentrations, higher order complexes such as $[Ag(CN)_3]^{2-}$ and $[Ag(CN)_4]^{3-}$ may be formed (Lorösch 2001).

Figure 2.4 Potential-pH diagram for the Ag-CN-H_2O system at 25 ºC



Osseo-Asare *et al.*,1984 taken from Lorösch, 2001.

2.1.1.3 The chemistry of iron cyanide

All ores treated in cyanidation contain iron minerals in various quantities. However, the solubility of metallic iron and most iron minerals is limited due to the formation of passivating surface films. Oxidic iron minerals such as hematite (Fe_2O_3), magnetite (Fe_3O_4), goethite (FeOOH), siderite ($FeCO_3$) and silicate iron minerals are virtually insoluble in aerated alkaline cyanide solution. Exceptions are melanterite ($FeSO_4.7H_2O$), which readily reacts with cyanide and ankerite ($Ca(Mg,Fe)(CO_3)_2$) which form ferrocyanides at pH < 10. Iron sulphides are far more susceptible to decomposition in alkaline cyanide solutions. This is discussed in Section 2.1.2 on sulphur species.

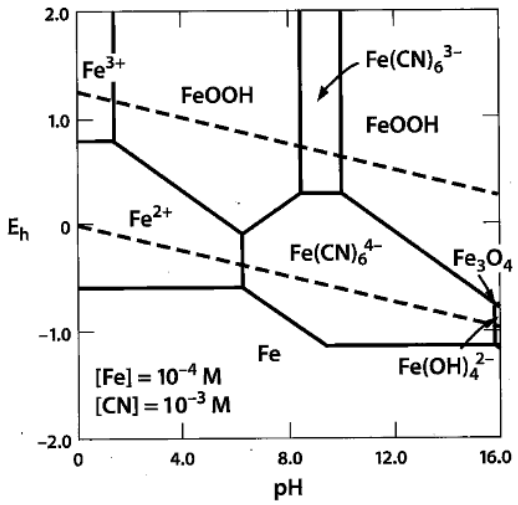
Soluble ferrous and ferric ions react with cyanide to form ferrocyanide and ferricyanide complexes respectively, according to Equation 2.10 (Lorösch, 2001).

Equation 2.10 Formation of ferrocyanide and ferricyanide

$$Fe^{2+} + 6\ CN^- \rightleftharpoons [Fe(CN)_6]^{4-} \quad (a)$$
$$Fe^{3+} + 6\ CN^- \rightleftharpoons [Fe(CN)_6]^{3-} \quad (b)$$

Thermodynamically, ferrocyanides are the predominant species under the typical pH and potential conditions of cyanidation (pH 10-11, ε < 0 V), as illustrated in the potential-pH diagram for the Fe-CN-H_2O system in Figure 2.5. Ferricyanides are only obtained in the presence of oxidants, are less stable and tend to be reduced to ferrocyanide.

Figure 2.5 Potential-pH diagram for the Fe-CN-H_2O system at 25ºC



Osseo-Asare *et al.*,1984 taken from Lorösch, 2001.

Under the alkaline conditions of cyanidation, soluble ferrous and ferric ions also form ferrous and ferric hydroxide precipitates. Some ferrous hydroxide precipitate may be dissolved by cyanide to form ferrocyanide and some may be oxidised by dissolved oxygen to form ferric hydroxide (Equation 2.11).

Equation 2.11 Reactions of ferrous hydroxide precipitate

$$Fe(OH)_2 + 6\ CN^- \rightleftharpoons [Fe(CN)_6]^{4-} + 2\ OH^- \quad (a)$$

$$2\ Fe(OH)_2 + ½\ O_2 + H_2O \rightleftharpoons 2\ Fe(OH)_3 \quad (b)$$

Ferric hydroxide precipitate is practically inert to cyanide. Therefore, aeration of an alkaline solution without the presence of cyanide may be used to reduce cyanide consumption in cyanidation.

2.1.1.4 The chemistry of copper cyanide

Copper occurs in a wide range of minerals in gold bearing ores. Copper minerals are far more soluble in cyanide than iron and have a major effect on the cyanide consumption of a gold

extraction plant.

Metallic copper is oxidised by dissolved oxygen in aerated alkaline cyanide solution to form insoluble cuprous cyanide, CuCN, on the surface of the copper, according to Equation 2.12 (a) (Lorösch, 2001). In a second step, the CuCN is dissolved under cyanidation to form the soluble cyanide complexes $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$, according to Equation 2.12 (b). In a well-agitated solution, the first reaction is rate determining. In the case of insufficient agitation or static leaching (heap leaching or vat leaching), an insoluble layer of CuCN may be formed on the copper surface considerably reducing any further copper dissolution.

Equation 2.12 Dissolution of copper

$$2\ Cu + O_2 + 3\ CN^- + H_2O \rightarrow 2\ CuCN + CNO^- + 2OH^- \quad (a)$$

$$CuCN + n\ CN^- \rightleftharpoons Cu(CN)_{n+1}^{n-},\ n = 1, 2, 3 \quad (b)$$

Copper minerals such as chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and bornite ($FeS\ 2Cu_2S\ CuS$) containing cuprous copper react directly with cyanide ions to form cuprous cyanide complexes. Chalcocite reacts according to Equation 2.13 (Lorösch, 2001).

Equation 2.13 Reaction of chalcocite with cyanide

$$Cu_2S + 6\ CN^- \rightarrow 2\ Cu(CN)_3^{2-} + S^{2-}$$

The sulphide ions are oxidised to either thiosulphate or sulphate or react with cyanide to form thiocyanate (see Section 2.1.2 on sulphur species).

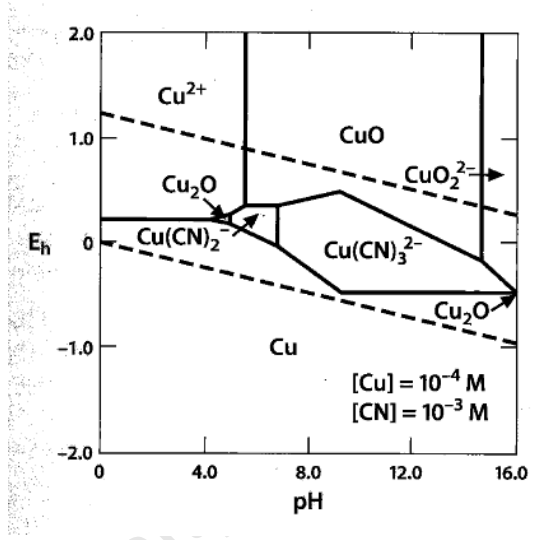
Cupric minerals or salts are reduced to form cuprous cyanide compounds, since cupric cyanide complexes are unstable, and cyanide is simultaneously oxidised to form cyanogen, $(CN)_2$ which is a pseudohalogen (Equation 2.14 (a)). Cyanogen then disproportionates in the presence of alkali to cyanide and cyanate (Equation 2.14 (b)).

Equation 2.14 Reduction of cupric minerals or salts to cuprous cyanide

$$2\ Cu^{2+} + 8\ CN^- \rightarrow 2\ Cu(CN)_3^{2-} + (CN)_2 \quad (a)$$
$$(CN)_2 + 2\ OH^- \rightarrow CNO^- + CN^- + H_2O \quad (b)$$

Metallic copper or copper minerals dissolve as cuprous cyanide complexes; $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$. According to the potential-pH diagram for the Cu-CN-H_2O system shown in Figure 2.6, $[Cu(CN)_3]^{2-}$ is the dominant species under the conditions of gold dissolution (pH 10-11, ε < 0 V).

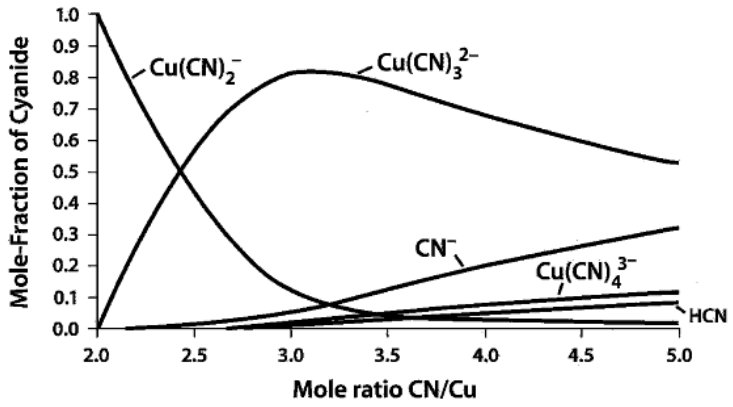
Figure 2.6 Potential-pH diagram for the Cu-CN-H_2O system at 25ºC



Osseo-Asare *et al.*,1984 taken from Lorösch, 2001.

The ratio between the different complexes depends on the pH, temperature and the concentrations of dissolved copper and cyanide. The distribution of cyanide among the various forms may be calculated for given total concentrations of cyanide and copper and for given pH values using the equilibrium constants. Figure 2.7 shows the distribution of cyanide among the copper cyanide complexes as a function of molar ratio CN/Cu at pH 10 for a total copper concentration of 10^{-3} mol/L (64 ppm). It illustrates the typical behaviour of copper cyanide species as the free cyanide concentration is increased. If the CN/Cu molar ratio is 2:1 or less in an alkaline pH, the cyanide in solution is present almost entirely as $[Cu(CN)_2]^-$. As the CN/Cu ratio rises, the proportion of $[Cu(CN)_2]^-$ drops, while that of $[Cu(CN)_3]^{2-}$ rises quickly to reach a maximum and that of $[Cu(CN)_4]^{3-}$ rises slowly.

Figure 2.7 **Calculated distribution of cyanide among the copper cyanide complexes, free cyanide and $HCN_{(aq)}$ as a function of the molar ratio CN/Cu using a copper concentration of 10^{-3} mol/L (64 ppm) and pH 10**



Griffiths *et al.*, 1987 taken from Lorösch, 2001.

2.1.1.5 The chemistry of zinc cyanide

Gold bearing ores do not contain metallic zinc but may contain a variety of zinc minerals, which react with cyanide to form $[Zn(CN)_4]^{2-}$. According to Lorösch (2001), sulphidic zinc minerals like sphalerite (ZnS) and oxidic zinc minerals like zincite (ZnO), willemite (Zn_2SiO_4) and smithsonite ($ZnCO_3$) dissolve with cyanide according to the reactions in Equation 2.15 (a-d).

Equation 2.15 **Reaction of zinc minerals with cyanide**

$$ZnS + 4\ CN^- \rightleftharpoons Zn(CN)_4^{2-} + S^{2-} \quad (a)$$

$$ZnO + 4\ CN^- + H_2O \rightleftharpoons Zn(CN)_4^{2-} + 2\ OH^- \quad (b)$$

$$Zn_2SiO_4 + 8\ CN^- + H_2O \rightleftharpoons Zn(CN)_4^{2-} + SiO_3^{2-} + 2\ OH^- \quad (c)$$

$$ZnCO_3 + 4\ CN^- \rightleftharpoons Zn(CN)_4^{2-} + CO_3^{2-} \quad (d)$$

Zinc minerals also dissolve in the presence of hydroxide ions to form zincate according to Equation 2.16.

Equation 2.16 **Reaction of zincite with hydroxide ions**

$$ZnO + 2\ OH^- \rightleftharpoons ZnO_2^{2-} + 2\ H_2O$$

The presence of hydroxide ions also promotes the formation of zincate from zinc cyanide complexes, which liberates bound cyanide ions according to Equation 2.17.

Equation 2.17 Reaction of zinc cyanide with hydroxide ions

$$Zn(CN)_4^{2-} + 4\ OH^- \rightleftharpoons 4\ CN^- + ZnO_2^{2-} + 2\ H_2O$$

A large hydroxide concentration will shift this reaction to the right, promoting the liberation of free cyanide. This is the mechanism whereby zinc cyanide complexes dissolve gold during cyanidation (Lorösch, 2001).

2.1.1.6 The stability of base metal cyanide complexes

Metal cyanide complexes may be grouped into three categories based on their stability; strong, moderate and weak metal cyanide complexes (Table 2.1). Strong cyanide complexes are formed with metals such as iron, cobalt, gold, platinum, and palladium, and have overall stability constants (log of cumulative stability constant) greater than approximately 30. Moderate cyanide complexes are formed with copper, nickel, and silver and have stability constants between 20 and 30. Weak metal cyanide complexes with zinc, cadmium and lead have stability constants less than approximately 20 (Marsden and House, 2006).

Table 2.1 Overall stability constants of strong, moderate and weak mono-cation cyanide complexes

Metal cyanide complex classification	Cyanide complex	Log of cumulative stability constant	Reference
Strong	$[Co(CN)_6]^{3-}$	log β_6 = 64.0	[Smith and Martell, 1970]
	$[Pd(CN)_4]^{2-}$	log β_4 = 51.6	[Sillen and Martell, 1970]
	$[Fe(CN)_6]^{3-}$	log β_6 = 43.6	[Smith and Martell, 1976]
	$[Fe(CN)_6]^{4-}$	log β_6 = 35.4	[Sillen and Martell, 1976]
	$[Pt(CN)_4]^{2-}$	log β_4 = 41.0	[Sillen and Martell, 1970]
	$[Au(CN)_2]^{-}$	log β_2 = 39.3	[Sillen and Martell, 1970]
	$[Hg(CN)_2]^{A}_{(aq)}$	log β_2 = 32.8	[ASTM D-6696-05]
Moderate	$[Ni(CN)_4]^{2-}$	log β_4 = 30.22	[Smith and Martell, 1976]
	$[Cu(CN)_2]^{-}$	log β_2 = 24.00	[Lurje,1971]
	$[Cu(CN)_3]^{2-}$	log β_3 = 28.60	[Lurje,1971]
	$[Cu(CN)_4]^{3-}$	log β_4 = 30.30	[Lurje,1971]
	$[Ag(CN)_2]^{-}$	log β_2 = 20.48	[Marsden and House, 2006]
	$[Ag(CN)_3]^{2-}$	log β_3 = 21.40	[Marsden and House, 2006]
Weak	$[Cd(CN)_3]^{-}$	log β_3 = 16.65	[Marsden and House, 2006]
	$[Cd(CN)_4]^{2-}$	log β_4 = 17.92	[Marsden and House, 2006]
	$[Zn(CN)_2]_{(aq)}$	log β_2 = 11.07	[Marsden and House, 2006]
	$[Zn(CN)_3]^{-}$	log β_3 = 16.05	[Marsden and House, 2006]
	$[Zn(CN)_4]^{2-}$	log β_4 = 19.62	[Marsden and House, 2006]
	$[Pb(CN)_4]^{2-}$	log β_4 = 10.30	[Sillen and Martell, 1964]
	$[Hg(CN)_4]^{2-B}$	log β_4 = 6.22	[ASTM D-6696-05]

Adapted from Smith and Martell, 1976; Sillen and Martell, 1964 and 1970; ASTM D-6696-05 2006; Marsden and House, 2006 and Lurje,1971

[A] $[Hg(CN)_2]_{(aq)}$ may be recovered by the available cyanide methods ASTM D-6888-04 or US-EPA OIA 1677 provided the second recommended ligand exchange reagent is used.

[B] Refers to the stepwise dissociation: $[Hg(CN)_4]^{2-} \leftrightarrow Hg(CN)_2 + 2CN^-$.

Ferro- and ferricyanide complexes can form double salts with a variety of cations such as sodium, potassium, calcium, ammonium and many other metal ions. Generally, the alkali metal, alkaline earth metal and ammonium ferro- and ferricyanides are soluble in water, while the heavy metal salts are insoluble (see Table 2.2). The Fe(II) cyanide complex, $[Fe(CN)_6]^{4-}$, which is common to all gold leaching circuits, forms a large number of mixed and bridged cyanide salts of varying solubility. A typical example of these double salts that occurs in process effluents is “Prussian Blue”, the insoluble Fe(II)/Fe(III) salt, $Fe_4(Fe(CN)_6)_3$. The formation and solubility of these salts is an important consideration in effluent disposal and treatment.

Table 2.2 Solubility products for selected metal cyanide compounds

Chemical formula	pK_{sp}	Reference
CuCN	19.49	[Lurje,1971]
Ag(CN)	15.66	[Marsden and House, 2006]
$Na_4[Fe(CN)_6]$	1.26	[Lorösch, 2001]
$K_4[Fe(CN)_6]$	0.57	[Lorösch 2001]
$Ca_2[Fe(CN)_6]$	-0.86	[Lorösch, 2001]
$K_3[Fe(CN)_6]$	-0.67	[Lorösch, 2001]
$Cu_2[Fe(CN)_6]$	17	[Lorösch, 2001]
$Cu_3([Fe(CN)_6])_2$	24.5	[Lorösch, 2001]
$Fe_2[Fe(CN)_6]$	14.14	[Lorösch, 2001]
$Fe_4([Fe(CN)_6])_3$	40.52	[Sillen and Martell,1970]

Adapted from Marsden and House, 2006; Lorösch, 2001 and Sillen and Martell, 1970.

2.1.2 Sulphur species

Iron sulphides are prone to decompose in alkaline cyanide solution to form iron cyanide complexes and various sulphur species. Pyrrhotite (Fe_7S_8) is the most reactive iron sulphide, followed by marcasite (FeS_2 with orthorhombic crystal structure), arsenopyrite (FeAsS), and pyrite (FeS_2 with cubic crystal structure) (Marsden and House, 2006). Pyrrhotite contains one loosely bound sulphur atom, which decomposes in alkaline solution to form sulphide ions. With intense aeration the sulphide will react to form thiosulphate and sulphate according to Equation 2.18 (a) and (b) (Lorösch, 2001).

Equation 2.18 Formation of thiosulphate and sulphate

$$2\ S^{2-} + 2\ O_2 + H_2O \rightleftharpoons S_2O_3^{2-} + 2\ OH^- \quad (a)$$
$$S_2O_3^{2-} + 2\ OH^- + 2\ O_2 \rightleftharpoons 2\ SO_4^{2-} + H_2O \quad (b)$$

Other intermediate oxidised sulphur species such as dithionate ($S_2O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$) and pyrosulphate ($S_2O_7^{2-}$) also form under various conditions (Hewitt *et al.*, 2009).

With less oxygen present, the sulphides will preferably react with cyanide to form thiocyanate according to Equation 2.19, resulting in an increase of cyanide consumption.

Equation 2.19 Formation of thiocyanate

$$2\ S^{2-} + 2\ CN^{-} + O_2 + 2\ H_2O \rightleftharpoons 2\ SCN^{-} + 4\ OH^{-}$$

2.2 CYANIDE CLASSIFICATION

The categories of cyanide compounds illustrated in Figure 2.8 are important from an environmental (toxicity) and analytical viewpoint (ASTM D-6696-05, Lorösch 2001, International Cyanide Management Institute (ICMI), 2011).

Figure 2.8 Classification of cyanide compounds

Cyanide type	$HCN_{(g)}$, $HCN_{(aq)}$	CN^-	Pb, Zn, Cd, Ag	Cu			Ni, Hg	Fe(II), Fe(III)	Co, Au, Pt, Pd	SCN^-	CNO^-
				4^{th} CN	3^{rd} CN	2^{nd} CN					
Free cyanide	■	■									
Titratable cyanide		■	■	■							
Cyanide available to leach Au		■	■	■	■						
Available cyanide	■	■	■	■	■	■					
WAD* cyanide	■	■	■	■	■	■	■				
SAD# cyanide								■	■		
Total cyanide	■	■	■	■	■	■	■	■	■		
Degeneration products										■	■

* Weak Acid Dissociable, # Strong Acid Dissociable

2.2.1 Free cyanide

Free cyanide refers to CN^-, $HCN_{(aq)}$ and $HCN_{(g)}$. It is the most toxic form. In practice 'free cyanide' is one of the most abused terms. Without matrix separation, there is no method available that gives the true, accurate value for the cyanide thus defined, when metals are present. Most methods include all cyanide bound in weak comp lexes, such as those of zinc and part of the cyanide bound in moderate complexes, such as those of copper. Copper cyanide exists in solution as the di, tri, and tetracyano complexes. Although the overall stability of the complexes is moderately high, the third and fourth cyanide ligands are weakly held. For example, the binding constant of the fourth cyanide would be $\log \beta_4 - \log \beta_3 = 1.1$ log units.

2.2.2 Titratable cyanide

Titratable cyanide is defined as the cyanide ion, the cyanide bound to lead, zinc, cadmium and silver, as well as the fourth cyanide bound in cuprous cyanide. The silver di and tricyano complexes

are titratable but not the final cyanide as AgCN precipitates. (Breuer and Rumball, 2007 and Breuer and Henderson, 2010).

2.2.3 Cyanide available to leach gold

According to literature the cyanide that is actually available to leach gold is the cyanide ion, the cyanide bound to lead, zinc, cadmium and silver, as well as the fourth and third cyanide bound in cuprous cyanide (Marsden and House, 2006). The gold leach rate for the third cyanide complexed with copper however is much lower than for free cyanide (Breuer, 2005).

2.2.4 Weak Acid Dissociable (WAD) cyanide

Weak Acid Dissociable (WAD) cyanide refers to weak or moderately stable metal cyanide complexes that dissociate at a moderate pH of 4.5-6 to release free cyanide and so are potentially toxic to humans and animals. These include the cyanide complexes of lead, zinc, cadmium, silver, copper and nickel with stability constants less than approximately 20, as well as free cyanide. Mercury is often referred to as a WAD cyanide species, the fourth and third cyanides of the tetracyano complex are bound such they dissociate, however $Hg(CN)_2(aq)$ is a strong complex (Table 2.1) and hence the remaining two cyanides are not expected to dissociate under WAD cyanide conditions. Even in the neutral pH range of most surface waters, WAD metal cyanide complexes can dissociate sufficiently to be environmentally harmful if present in high enough concentrations. WAD cyanide determination provides a reasonable estimate of toxicity. The term WAD cyanide refers to the sum of both WAD and free cyanide.

2.2.5 Available cyanide

Available Cyanide is a class of cyanide species that are defined by the dissociation and release of free cyanide under the action of ligand exchange reagents. Such compounds are thought to be potentially bioavailable in the environment and so this measurement also is considered to provide a conservative estimate of cyanide toxicity. In water, available cyanide includes free cyanide and the metal cyanide complexes of lead, zinc, cadmium, silver, copper, nickel and mercury.

2.2.6 Strong Acid Dissociable (SAD) cyanide

Strong Acid Dissociable (SAD) cyanide refers to strong metal cyanide complexes that require strongly acidic conditions in order to dissociate (pH<2). These include the cyanide complexes such

as those of ferrous, ferric, cobalt, gold, platinum and palladium (palladium and mercury are sometimes categorised as WAD cyanide species (Lotz, 2001, ASTM D-6696-05)). These complexes are very stable even under mildly acidic conditions. However, both ferrocyanides and ferricyanides decompose to release free cyanide when exposed to direct ultraviolet light in aqueous solutions, according to Equation 2.20 but not sufficiently in turbid, shaded surface waters to present any significant danger of toxicity.

Equation 2.20 Decomposition of ferrocyanide by ultraviolet light

$$[Fe(CN)_6]^{4-} + H_2O \xrightarrow{h\nu} [Fe(CN)_5\ H_2O]^{3-} + CN^-$$

2.2.7 Total cyanide

Total cyanide is an analytical term that refers to the sum of all forms of cyanide that dissociate and release free cyanide when refluxed under strongly acidic conditions. It includes all free cyanide, all dissociable cyanide complexes and all strong metal cyanide including ferrocyanide ($[Fe(CN)_6]^{4-}$), ferricyanide ($[Fe(CN)_6]^{3-}$), and portions of hexacyano cobaltate $[Co(CN)_6]^{3-}$ and those of gold and platinum. Double salts such as $Fe_4[Fe(CN)_6]_3$ (Prussian blue), organo-cyanides (nitriles) are included to various degrees depending on the particular method. Only the related or derived compounds cyanate (CNO^-) and thiocyanate (SCN^-) are excluded from the definition of total cyanide.

2.2.8 Other cyanide complexes

Other cyanide related compounds such as thiocyanate (SCN^-) and cyanate (CNO^-). Thiocyanate dissociates under weak acidic conditions, but is typically not considered to be a WAD species because it has similar complexing properties to cyanide. Thiocyanate is approximately seven times less toxic than hydrogen cyanide to humans based on concentrations of critical toxicity, but is very irritating to the lungs, as thiocyanate chemically and biologically oxidizes into carbonate, sulphate and ammonia. The oxidation of cyanide, either by natural processes or by the destruction treatment of effluents produces cyanate. Cyanate is also less toxic than hydrogen cyanide, and hydrolyses to ammonia and carbon dioxide.

2.3 CYANIDE MEASUREMENT TECHNIQUES

There is a proliferation of methods for the analysis of cyanides, probably due to the toxicity of the species, as well as the economic and environmental implication of cyanide monitoring on gold plants. The methods vary in chemistry, complexity and accuracy.

Cyanide analysis has been the subject of several reviews. Bark and Higson (1963), Pohlandt *et al.* (1983), Singh and Wasi (1986) and Barnes *et al.* (2000) reviewed various titrimetric, colorimetric, electrometric, radiochemical and chromatographic methods that are suitable for the detection and determination of cyanides present in a variety of matrices. The selectivity of the methods and the extent to which they enable one to distinguish between free, WAD and total cyanide was found to be method dependent. Most methods for the determination of ionic cyanide in process streams and effluents were reported to be liable to interference from metal cyanide complexes.

A distinction should be made between standard methods and methodologies. The term standard method is used for nationally or internationally recognized methods with a defined accuracy and precision and a tightly prescribed procedure. Examples would be International Organization for Standardization (ISO), American Society for Testing and Materials (ASTM), United States Environmental Protection Agency (US-EPA), South African National Standard (SANS), American Public Health Association (APHA), Deutsches Institut für Normung (DIN) and Office of International Activities (OIA). A methodology is a generally accepted way of quantifying certain analytes under a wide range of conditions and applications without knowledge of its accuracy, precision and robustness. Standard methods are typically preferred for regulatory purposes even if they are known to have shortcomings in certain applications. Free, WAD and total cyanide standard methods and methodologies as published by ICMI, ISO, ASTM International, US-EPA, SANS, APHA, DIN and OIA are listed in Table 2.3 and discussed below.

2.3.1 Free cyanide standard methods and methodologies

Most available methods do not measure free cyanide accurately, according to its true definition, in the presence of base metals. They include up to four of the cyanide ions bound in weak metal cyanide complexes, such as those of zinc, and up to two of the cyanide ions bound in moderate metal cyanide complexes such as those of copper. Only those methods that include a matrix separation step come close to the textbook definition; such as ASTM D-4282 and ASTM D-7237.

ASTM D-4282 describes the micro diffusion of hydrogen cyanide from a static sample (pH 6 and room temperature) into a sodium cyanide solution where it is accepted as CN^-. Cyanide is thus separated from the matrix for accurate determination without the presence of interferents. A slight over-detection of cyanide may result from the liberation of WAD cyanide at pH 6. ASTM D-7237-06 is a modification of this method for aquatic cyanide ranging between 2 and 500 ppb, in aqueous wastewater or effluent.

Cyanide Ion Selective Electrodes (CN-ISE's) are usually solid-state electrodes (silver iodide or a silver iodide/silver sulphide), which develop a potential across the membrane proportional to the concentration of cyanide in solution. Silver sulphide electrodes are not recommended for use at pH values lower than pH 9 due to the interference of the protons (Lotz, 2001). CN-ISE electrodes are also influenced by various metal ions like copper, as well as sulphide and oxidised sulphur species (Gattrell *et al.* 2001, Naumann *et al.* 1971).

Amperometry and polarography are a sub-class of voltammetry, where the current is measured at a fixed and changing potential, respectively. Amperometry is the measurement of a steady-state current in an electrolytic cell that is due to the oxidation or reduction of the analyte species. In the presence of an applied potential, a limiting current is established from reaction of cyanide with a working electrode, which is proportional to the concentration of cyanide. According to Crundwell and Jensen (1994), appropriate electrodes may be made of metals such as gold, silver or copper, or semiconductors such as copper sulphide. The electrode may either be stationary or rotating. Mc Closkey (1961) showed that a linear amperometric response is produced for trace amounts of cyanide ranging from 1-11 ppb and sensitivity was increased by increasing the electrode rotation speed (decreasing the diffusion path by disturbing the boundary layer) or size of the cathode and anode surface area (increasing total current for same potential). Polarography makes use of the dropping mercury-working electrode (Henze, 2001). Mercury instantly forms a mercury-cyano complex plus two electrons when it comes into contact with cyanide. These electrons create the current measured, which is proportional to the concentration of the available cyanide in the sample (Canterford, 1975).

The most common method for the analytical determination of free cyanide is silver nitrate titration. It is also one of the oldest cyanide determination methods, dating back to its initial discovery by Liebig in 1851. As cyanide is titrated with standard silver nitrate ($AgNO_3$), the addition of silver ions complexes available free cyanide ions to form the soluble cyanide complex $[Ag(CN)_2]^-$, until an excess of silver ions indicates the endpoint of the titration. Excess silver may be detected by an indicator such as potassium iodide or rhodanine or by potentiometry. Potentiometric titration is more

accurate than colorimetric endpoint determination as a more easily identifiable peak signal is produced. However, standard methods only exist for endpoint detection by the silver-sensitive indicator, p-dimethylaminobenzalrhodanine, which immediately turns from yellow to a salmon colour. Copper cyanide and sulphur species, such as thiosulphate, are also titrated by silver nitrate and often make endpoint detection difficult and inaccurate. In the presence of base metals, all cyanide associated with $Zn(CN)_x$ and the fourth cyanide associated with $[Cu(CN)_4]^{2-}$ is included in the measurement (Breuer and Henderson, 2010).

Free cyanide determination by colorimetry is achieved by reaction of the cyanide ion with chloramine-T at pH<8 to form cyanogen chloride which reacts with pyridine-barbituric acid to form a red-blue compound which has a maximum colour absorbance in aqueous solution between 575 and 582 nm. Many of the standard methods use a colour formation step as a means of final quantification of separated free cyanide from matrix. Colorimetry is sometimes used on mine sites and laboratories without matrix separation, to quantify free cyanide directly in the original matrix, and is called direct colour formation. This is not a recommended methodology due to the strong likelihood of interferents (Lotz, 2001).

SANS/ISO 14403 relies on the release of free cyanide during a distillation step. It is a modification of a method for total cyanide where UV B is applied to release cyanide bound by iron at a pH of 3.8. The 'free' cyanide method however omits UV irradiation but retains buffering the sample to pH 3.8 which would lead to an over-quantification of free cyanide. The validity of this method is therefore questionable.

2.3.2 WAD cyanide standard methods and methodologies

WAD cyanide may either be liberated from associated metals by creating an environment conducive to liberation (acidic pH adjustment and reflux) or by using a ligand exchange reagent.

The distillation method according to ASTM, ISO/DIS 6703/2 or DIN 38504 Part 13.2 liberates WAD cyanide by adjusting the pH of 4.5 and heating for an hour, so that hydrogen cyanide is carried in an air stream and absorbed into a caustic soda solution for free cyanide analysis by silver nitrate titration or colorimetry. Though the standard test methods recommend a distillation time of 60 minutes, AMIRA has shown that high copper levels (the cracking of precipitated CuCN) will take much longer; up to 4 hours.

ASTM D-6888-04, with the US-EPA equivalent OIA-1677 are approved Standard Test methods based on the use of ligand exchange reagents to liberate WAD cyanide. They recommend two ligand exchange reagents to liberate cyanide from the aqueous metal cyanide species of zinc, cadmium, copper and nickel, and if necessary from mercury. Ligand exchange reagents do not liberate cyanide from CuCN. Liberated cyanide is measured by amperometry.

According to ICMI, manual distillation or Flow Injection Analysis (FIA) inline ligand exchange with amperometric finish are recommended methods of choice as interfering effects of salinity and other matrix parameters are less significant.

Picric acid (trinitrophenol) can be used in a colorimetric procedure to determine the concentration of WAD cyanide, after the addition of a ligand exchange reagent. In the presence of free cyanide, picric acid is reduced to the orange coloured isopurpuric acid while cyanide is oxidised to cyanate. The colour intensity of the orange coloured isopurpuric acid is directly proportional to the concentration of free cyanide originally present in the sample. No associated standard method exists for the picric acid method. Solutions of picric acid are safe for ordinary laboratory use. However, in dry form the acid, and especially some of its salts, have explosive properties (Iamarino, 1989).

2.3.3 Total cyanide standard methods and methodologies

The standard methods for total cyanide quantification are based on either batch distillation or FIA with UV irradiation.

During batch-wise manual distillation (ISO/DIS 6703, DIN 38405 Part 13.1: 1981-02, ASTM D-2036, EPA 9010, APHA 4500-CN, SABS 204), strongly acidic conditions and elevated temperatures liberate the cyanide ion from stable cyanide complexes such as ferricyanide and ferrocyanide. After separation by distillation, hydrogen cyanide is quantified in sodium hydroxide solution by titration, potentiometry or colorimetry. This technique is time-consuming, costly and low concentration results are often unreliable.

Segmented Flow Injection Analysis (SFIA) (ASTM D-4374) is a continuous, inline system where samples are injected or drawn up into an acidic carrier stream. Samples are separated by an air bubble, hence the term ‘segmented’ so as to prevent linear dispersion. They are then exposed to UV irradiation for the complex excitation and breakdown. Micro distillation or micro-diffusion yields

hydrogen cyanide which is then quantified colorimetrically or amperometrically. This is a faster process than distillation (20 minutes), but only worthwhile for at least 10 to 12 samples because of the time-consuming set-up phase. This method is very accurate and precise at extremely low levels.

Both distillation and UV irradiation standard methods measure free cyanide, Zn/Cd/Cu/Ni/Ag/Fe$(CN)_x$, and parts of Au/Co/Pt/Pd$(CN)_x$, (only 20-40% cyanide bound to cobalt is recovered).

According to Barnes *et al.* (2000) High Performance Liquid Chromatography (HPLC) is the only methodology that recovers all Au/Co/Pt/Pd$(CN)_x$. A small plug of sample containing cyanide is injected into a flowing acetate/sodium hydroxide-based eluant which passes through a stationary, resin phase. Cyanide may be separated from sulphur adducts, metal cyanide complexes and from inorganic anions by their different affinities for the resin. After separation, cyanide is determined by amperometry and the metal cyanide complexes are determined by UV spectrophotometry (215 nm).

Table 2.3 Standard methods and methodologies for free, WAD and total cyanide measurement

Analyte	Standard method/ methodology	Generic steps contained	DL	Comments
Free Cyanide	APHA 4500-CN–D, US EPA 9014	$AgNO_3$ titration > p-dimethylamino-benzal-rhodanine indicator	1.0 mg/L	Interferences: copper, sulphide. Sulphide may be removed by precipitation with lead acetate/carbonate.
	APHA 4500-CN–E, US EPA 9014, ASTM D-4165-00	pH buffer > colorimetry (CNCl, pH<8 and pyridine-barbituric acid, absorbance at 578 nm)	0.01 mg/L 0.005 mg/L (ASTM D-4165-00)	Interferences eliminated/reduced by distillation. Colour and turbidity can interfere.
	APHA 4500-CN–F, US EPA 9213	Potentiometric ISE	0.05 mg/L	Interferences: sulphide, temp changes, colloids if not filtered.
	ASTM D-4282	Diffusion of $HCN_{(g)}$ at pH 6 and room temp > NaOH receptacle > colorimetry (CNCl, pH<8 and pyridine-barbituric acid, absorbance at 578 nm)	0.01 mg/L	Interferences: decomposition of Fe(CN)x unless precipitated with Cd(II) or diffusion performed in dark.
	ASTM D-7237	Aquatic free CN > FIA buffer pH 6-8 > direct membrane diffusion > amperometry	0.002 mg/L	Interferences: sulphide diffusion through membrane unless removed by precipitation with lead acetate/carbonate.
	ISO/SANS 14403	FIA acidification > direct distillation > scrubbing > colorimetry (CNCl, pH<8 and pyridine-barbituric acid, absorbance at 578 nm)	0.01 mg/L	Method validity questionable due to over-quantification of free cyanide (at pH 3.8 WAD cyanide will have dissociated).
	Methodology	Amperometry	0.0002 mg/L	Interferences: hypochlorite, sulphide, thiosulphate.
	Methodology	Polarography	0.01 mg/L	
	Methodology	$AgNO_3$ titration > miscellaneous methodologies		
	Methodology	Direct colour formation		
WAD cyanide	ASTM D-2036, ISO/DIS 6703/2,	Manual distillation pH 4.5 > potentiometry or colorimetry	0.05 mg/L	Better results than ASTM D-4374 in presence of high copper

	DIN 38405 Part 13.2: 1981-02			concentration.
	ASTM D-4374	SFIA inline micro-distillation pH 4.5 > colorimetry (CNCl, pH<8 and pyridine-barbituric acid, absorbance at 578 nm)	0.0005 mg/L	Interferences: turbidity and colour contributing substances, >10mg/L sulphides (removed with dilution or lead acetate/carbonate), some metal cations (eg. >1 mg/L mercury), fatty acids.
	US-EPA OIA-1677, ASTM D-6888-4	FIA inline ligand exchange > amperometry	0.002-0.400 mg/L dilute higher concs	Interferences: sulphides (removed with lead acetate/carbonate), >1000 mg/L carbonate releases CO_2 which interferes with amperometric detector.
	Methodology	Ligand exchange > colorimetry (picric acid, absorbance at 520 nm)	0.02-3 mg/L dilute higher concs	Interferences: >0.1 mg/L sulphides (removed with lead acetate/carbonate), high concentrations of thiocyanate, cyanate and thiosulphate. Method requires close pH control between 9.0 and 9.5 for constant colour development.
Total Cyanide	ISO/DIS 6703, DIN 38405 Part 13.1: 1981-02, ASTM D-2036, US-EPA 9010, APHA 4500-CN, SABS 204.	Manual batch reflux-distillation > titration or colorimetry (CNCl, pH<8 and pyridine-barbituric acid, absorbance at 578 nm)	0.10 mg/L	Interferences: >0.02 mg/L sulphide ions, >1000 mg/L carbonate ions, >0.02 mg/L aldehydes, >20 mg/L total organically bound carbon.
	ASTM D-4374, US EPA 335.3	SFIA, inline UV irradiation, micro-distillation > colorimetry (CNCl, pH<8 and pyridine-barbituric acid, absorbance at 578 nm)	0.0005 mg/L (ASTM) 0.005 mg/L (US-EPA)	Interferences: turbidity and colour contributing substances, sulphides >10mg/L (removed with dilution or lead acetate/carbonate), nitrate-nitrite (removed with sulphamic acid), some metal cations (eg. >1 mg/L mercury), fatty acids, >1 mg/L thiourea, >100 mg/L cysteine), UV digestion of thiocyanates.
	Methodology	HPLC		

Some methods or methodologies have been developed into online plant analysers, while others are only suitable for laboratory use and require sophisticated laboratory equipment. Online analysers should be sufficiently robust to operate in a remote cabin on a gold plant and simple enough to be operated and maintained by plant personnel. The two most common commercialised online free cyanide analysers are based on potentiometric titration and amperometry and are discussed below in Section 2.5.

Standard laboratory methods all rely on separation of the analyte from the matrix in an attempt to remove interferences. They are developed for laboratory use where the highest possible accuracy should be obtained, with implementation by skilled laboratory technicians. They normally have an uncertainty margin of around 1% for simple sodium cyanide analysis, which can increase to 5% in the upper areas of the dynamic range of analysis from where linear amperometric response is achieved. Online analysers should be robust, require minimal supervision by trained staff and are not expected to exhibit the accuracy of a laboratory technique. Online instruments are therefore

simpler and do not include a matrix separation step. As a result the uncertainty margin is increased to 10%. Standard test methods are not developed for online instruments. Therefore if regulatory compliance is required, accredited laboratories utilising standard methods should be employed to validate any in-house or online analysis (Klein, 2001).

2.4 CYANIDE REGULATIONS

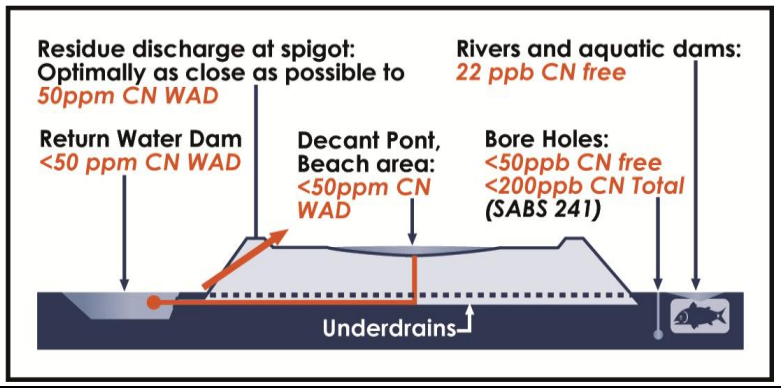
In May 2000, the United Nations Environment Programme (UNEP) and the International Council on Metals and the Environment (ICME) initiated the development of an international, globally based voluntary program designed to improve the management of cyanide at gold mines. This program soon became known as the "International Cyanide Management Code for the Manufacture, Transport and Use of Cyanide in the Production of Gold".

The International Cyanide Management Institute (ICMI) administers the Code. It is a non-profit corporation with a multi-stakeholder Board of Directors consisting of representatives from the gold mining industry, governments, non-governmental organizations, labour and cyanide producers.

The Code is intended to assist in the protection of human health and the reduction of environmental impacts associated with the use of cyanide. This is achieved by reducing the potential exposure of workers and communities to harmful concentrations of cyanide and limiting releases of cyanide to the environment. The Code includes routine monitoring requirements and numerical limits for free and WAD cyanide but not for other forms of cyanide such as total cyanide, cyanate, thiocyanate, cyanogens and SAD cyanide. The Code specifies the following WAD cyanide concentration limits, as illustrated in Figure 2.9:

- 50 ppm WAD cyanide in a tailings storage facility.
- 0.5 ppm WAD cyanide for effluents.
- 0.022 ppm free cyanide or 0.022 ppm WAD cyanide as surrogate in the post mixing zone of river discharge.

Figure 2.9 Cyanide concentration limits specified by ICMI



The residue concentration limit of 50 ppm is sufficiently protective of terrestrial life (birds, animals and humans) but is likely to be further reduced in the near future. Aquatic life requires a limit of three orders of magnitude lower, 0.03 ppm. The World Health Organisation recommends that water containing more than 0.010 ppm free cyanide should be rejected as unfit for public use (domestic supply).

Governments and local authorities often stipulate their own concentration limits. These can vary considerably depending on the region. For example, in Chile and Peru, the effluent limit is 1 ppm, in Bolivia the river discharge limit decreases from 0.5 ppm to 0.2 ppm further downstream and in Argentina the limit value is 0.1 ppm (Wikipedia, 2010). In Russia limits for total cyanide are stipulated. Some countries have instituted a progressive reduction in concentration limits. In Brussels the 50 ppm limit will drop to 25 ppm in 2013 and 10 ppm in 2018 (Rodriguez and Macias, 2009). By becoming a signatory, a company commits to follow the Code's principles and to implement its standards of practice. Gold plants using cyanide are required to measure WAD cyanide online and destroy WAD cyanide in excess of the applicable limits.

To date, thirty gold mining companies in thirteen countries are signatories to the International Cyanide Management Code (International Cyanide Management Institute, 2011).

Globally, there has not been a major environmental incident for more than a decade. This achievement is a tribute to the industry accepting responsibility for potential risks and implementing strategies to further reduce them (Mudder, 2007).

2.5 CYANIDE CONTROL

Cyanide contributes to 25% of the entire cost of gold extraction in certain applications. The efficient

control of cyanide addition to the leach circuit can be essential for economical operation of a gold plant. Online cyanide control can result in reduction of cyanide consumption by at least 5% with savings of up to 30% and reductions in soluble gold of at least half, compared to manual control (Lorösch 2001).

Typical cyanide control is carried out by measuring the cyanide concentration in the first leach tank, either manually every 2-12 hours or with an online instrument every 5-30 minutes. Cyanide consumption can vary significantly in a short period of time (<2 hours) due to a change in ore mineralogy. Therefore, as one would expect, the frequency of the online measurement and the elimination of human error, compared to manual sampling, facilitates tighter cyanide control to the set-point. This results in a cyanide cost reduction and less cyanide being discharged into the tailings stream, without compromising gold recovery.

Automated cyanide addition control algorithms require a frequent cyanide concentration input provided by an online instrument. The two most common free cyanide measurement techniques adopted for online analysers are potentiometric endpoint silver nitrate titration and amperometry.

2.5.1 Online free cyanide measurement by potentiometric silver nitrate titration

Potentiometric silver nitrate titration uses the potential measured by a silver wire in the titration solution as an indicator of changes in solution speciation as silver nitrate is added. Commercial instruments based on this technique are supplied by the South African company, Process Analytical Systems (Pty) Ltd, the German company, CyPlus GmbH and the Australian company, Orica Limited that bought Cyantific Instruments. A filter unit provides a solid-free leach solution from the leach pulp so that measurements are performed every 10-20 minutes and typically coupled with a cyanide control system and automatic dosage of the sodium cyanide solution. The efficient cyanide control reduces cyanide consumption by up to 30%, so that the instrument investment is paid off within a few months (Process Analytical, 2011, Orica Chemcials, 2011, Cyplus, 2011).

2.5.2 Online free cyanide measurement by amperometry

The Mintek Cynoprobe is the only commercially available online free cyanide analyser based on amperometry. The diffusion current arising from the oxidation of silver to dicyanoargentate(I) is measured in the presence of an applied potential, according to Equation 2.21.

Equation 2.21 Oxidation of silver to dicyanoargentate(I)

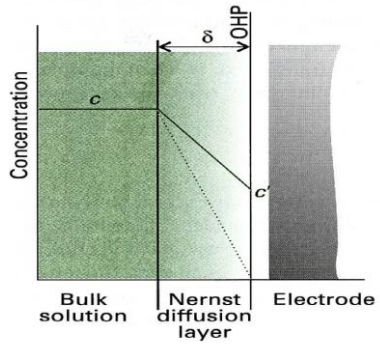
$$Ag + 2\ CN^- \rightleftharpoons Ag(CN)_2^- + e^-$$

The Cynoprobe electrolytic cell consists of a stationary, working silver electrode, stainless steel counter electrode and a Ag/AgCl reference electrode.

The rate of the reaction between silver and cyanide is mass transfer controlled. According to the Nernst diffusion layer model for mass transport the liquid adjacent to the solid electrode surface is assumed to be stationary. Mass transport through the stationary film, with thickness δ that is dependent on the state of flow of the liquid, is considered to be a diffusion and migration process. Diffusion is affected by temperature and the concentration gradient. Migration is affected by the presence of an electric field. Beyond the diffusion layer, mass transport is enhanced by means of convection involving movement of the liquid by stirring or other convective processes.

Figure 2.10 is a schematic representation of the Nernst diffusion layer model where the concentration of the reacting species is plotted as a function of distance from the reacting surface (Nicol, 2010 and Atkins, 1998).

Figure 2.10 A schematic representation of the Nernst diffusion layer model for mass transport



Taken from Atkins, 1998.

The mass transport rate of cyanide ions to the surface of the silver electrode due to diffusion is therefore dependent upon temperature, cyanide concentration and the degree of agitation. The migration of ions is dependent on the applied potential. The total current is also dependent on the surface area of the silver electrode. The current produced can therefore be expressed according to Equation 2.22.

Equation 2.22 Cynoprobe current equation

$$\text{Current} = f(T, [CN^-], A, E, \Delta)$$

T = temperature; $[CN^-]$ = cyanide concentration in solution; A = silver electrode surface area; E = applied potential; Δ= degree of agitation in the vessel; f = constant.

The Cynoprobe controls the solution measured to set-point temperature, assumes a constant silver electrode surface area within a two month period, measures at a specific applied potential and is installed in a vibration free environment, so that Equation 2.22 above may be simplified to Equation 2.23.

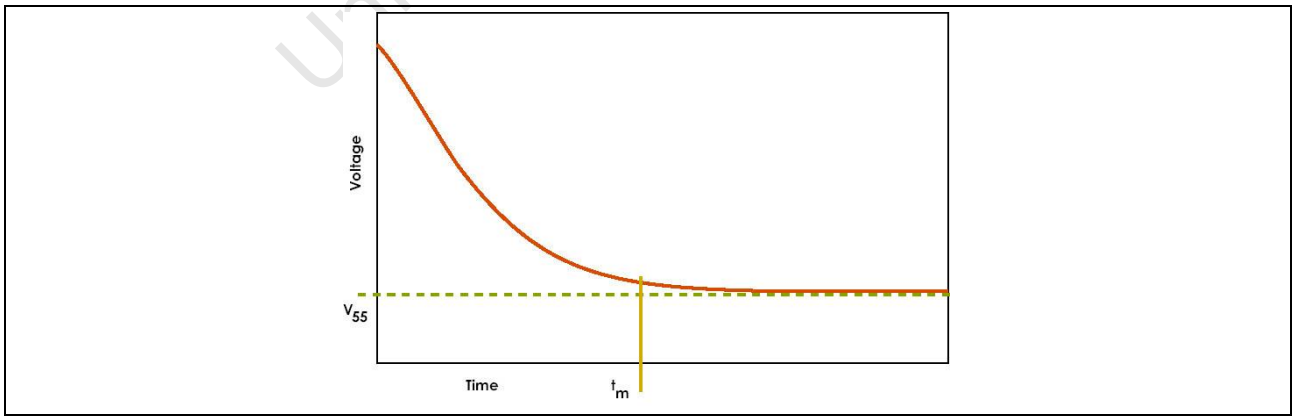
Equation 2.23 Simplified Cynoprobe current equation

$$\text{Current} = m\,[CN^-]$$

m represents a lumped parameter constant of the temperature, silver electrode surface area and degree of agitation.

The kinetics of electrode processes can be studied by measuring the resulting current (or voltage) over a certain period of time. As a voltage is applied to the Cynoprobe circuit, the current initially increases as cyanide ions react with silver at the electrode surface but it then decreases to reach a steady state value, where the rate of charge transfer becomes constant. A typical amperometric response at an applied voltage is shown in Figure 2.11. The Cynoprobe records the steady state voltage after a set time.

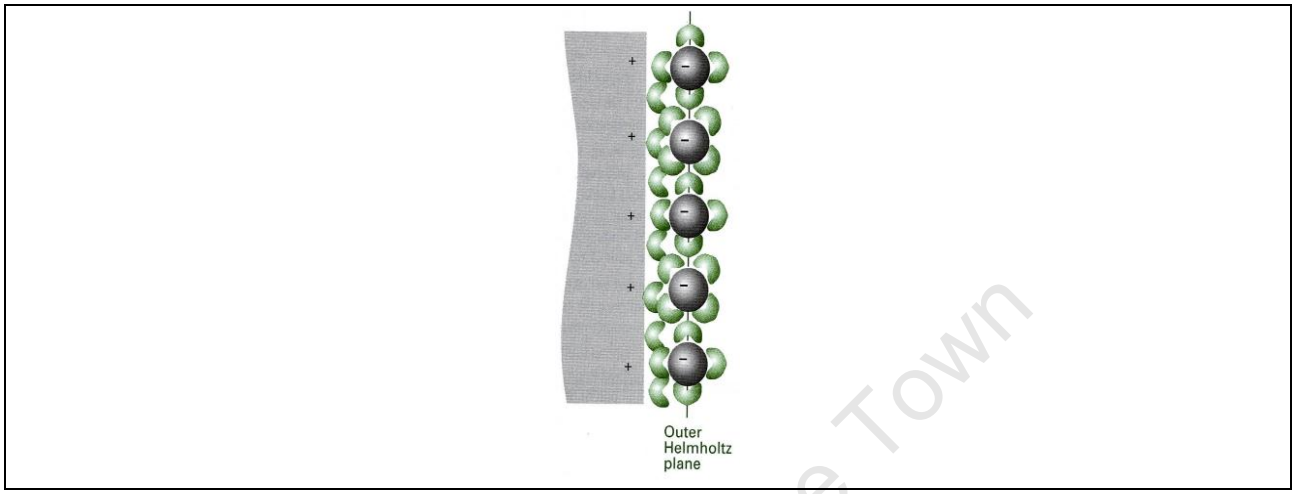
Figure 2.11 Cynoprobe voltage vs. time graph for cyanide measurement



The shape of the graph in Figure 2.11 can be explained by the build-up of charge on the silver electrode over time to form a boundary layer. As electrons leave the electrode it becomes positively charged relative to the solution nearby so that an electrical double layer forms consisting of positive

and negative charge. A simple model of the electrical double layer treats it as two rigid planes of charge, one plane, the outer Helmholtz plane (OHP), being due to the ions with their solvating molecules, the other being that on the electrode itself (Atkins, 1998), as shown in Figure 2.12.

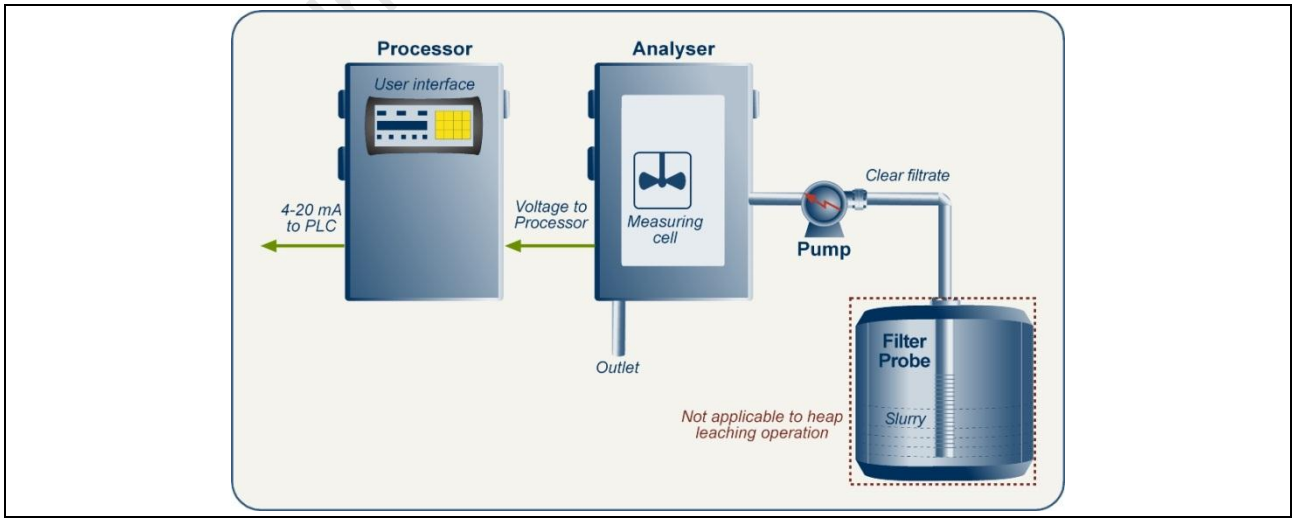
Figure 2.12 The Helmholtz model of the electrical double layer formed on the surface of an electrode



Taken from Atkins, 1998.

The Cynoprobe's sequence of operation for free cyanide measurement is shown in Figure 2.13. Leach tank slurry is filtered by a stainless steel filter probe and filter sock so that clear filtrate is supplied to the amperometric cell in the Analyser Unit. The resulting electrochemical signal is transferred to the Processor Unit so that an output cyanide concentration may be sent to the plant Programmable Logic Controller (PLC) to be used in a cyanide control algorithm.

Figure 2.13 A schematic diagram showing various components of the Cynoprobe



Amperometry is one of the most accurate methods to measure free cyanide over a wide

concentration range (Pihlar and Kosta, 1979). Various concentration ranges may be measured depending on the resistance of the circuit; namely 0.3-30 ppm, 1-100 ppm, 3-300 ppm 10-1000 ppm and 30-3000 ppm. A dilution step facilitates the measurement of higher cyanide concentrations such as 10 000 to 15 000 ppm.

The amperometric technique takes place on a microscopic scale so that the equilibrium between the free cyanides and the cyanides bound to metals such as copper does not change to the degree it does when silver nitrate is added during potentiometric titration.

2.6 CYANIDE DESTRUCTION

In the early days of cyanidation, cyanide destruction by natural degradation in the tailings ponds or dams was considered sufficient. However, the gold mining boom and the development of the International Cyanide Management Code in the year 2000, which specified stricter limits for the discharge of cyanides, made it necessary for gold mining companies to implement cyanide destruction to avoid environmental problems. Today, cyanide detoxification is one of the essential steps in the flow sheet of cyanidation, especially where abundant wildlife or aquatic discharges to the environment have to be considered.

Online measurement of the WAD cyanide concentration should be used together with process control algorithms to optimise cyanide destruction reagent consumption and guarantee effluent quality. Proper oxidant dosage control and monitoring of effluent concentration levels will ultimately result in less cyanide and post-destruction salts being discharged into the environment.

Many treatments involving biological, catalytic, electrolytic, chemical and photolytic methods may be used to destroy cyanide in gold leaching effluents (Young and Jordan 1995). The most widely used treatments involve the use of chemical oxidants. The most commonly adopted oxidants for cyanide oxidation are hydrogen peroxide, the persulphates and peroxymonosulphuric acid (Lorösch 2001).

There are several cyanide destruction processes that have been commercialised. The Hydrogen Peroxide Process and the SO_2/air INCO Process are the leading cyanide detoxification technologies. Sodium metabisulphite and hydrogen peroxide are often used together in a two-step addition method termed the Combinox Process. An overview of the most common cyanide destruction methods is discussed below.

2.6.1 The INCO SO_2/Air-Process

In the early 1980s the Canadian INCO group commercialised the process of combining SO_2 and air in the presence of a Cu(II) catalyst to destroy cyanide, according to Equation 2.24 (Botz, 2001).

Equation 2.24 Destruction of cyanide by INCO SO_2/Air-Process

$$CN^- + SO_2 + O_2 + H_2O \xrightarrow{\substack{Cu(II) \\ catalyst}} CNO^- + H_2SO_4$$

The oxidant in this process is oxygen from the air assisted by sulphur dioxide. Since the reaction proceeds via the formation of dissolved sulphite (SO_3^{2-}), SO_2 may be substituted by sodium sulphite (Na_2SO_3) or sodium meta-bisulphite $Na_2S_2O_5$. This process is effective for free and WAD cyanide, but only partially destroys thiocyanate.

2.6.2 Hydrogen peroxide detoxification

Copper catalysed hydrogen peroxide detoxification was developed simultaneously to the INCO Process in the late 1970s and early 1980s by Degussa. The non-catalysed oxidation of cyanide to cyanate can be considered a one-step reaction, according to Equation 2.25 (Lorösch 2001).

Equation 2.25 Destruction of cyanide by hydrogen peroxide

$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O$$

The addition of Cu(II) ions catalyses the cyanide oxidation. Copper sulphate is commonly used. The detailed mechanism of the copper catalysed hydrogen peroxide process is still unknown. The rate of detoxification is dependent on temperature, pH, copper catalyst concentration, hydrogen peroxide addition rate, and the cyanide type and concentration. The fastest rate of detoxification is said to be obtained at pH 10. The inclusion of 10 mg/L Cu increases the rate 2 to 3 fold, while a 20% excess of hydrogen peroxide will increase the rate by about 30%. Increasing the temperature also increases the reaction rate.

2.6.3 The Caro's acid process

The synthesis and oxidising properties of peroxymonosulphuric acid were first described in 1898 by

a German chemist Heinrich Caro; hence the name Caro's acid (see Equation 2.26). The term Caro's acid describes the equilibrium mixture of peroxymonosulphuric acid, hydrogen peroxide, sulphuric acid and water (Lorösch 2001).

Equation 2.26 Synthesis of peroxymonosulphuric acid

$$H_2O_2 + H_2SO_4 \rightleftharpoons H_2SO_5 + H_2O$$

As a result of its relative instability (a shelf life of a day), its large-scale application and commercialisation was only resolved in the early 1990s. In the laboratory, high grade 'cold' Caro's acid is prepared by an isothermal process with efficient heat removal ensuring the temperature does not exceed 15ºC. In operating plants, low grade 'hot' Caro's acid is produced in situ in an adiabatic process where >85% sulphuric acid and >50% hydrogen peroxide are mixed rapidly in a small-volume high throughput static mixer without cooling.

Caro's acid is the most efficient commercialised oxidant for cyanide destruction. It reacts very specifically with cyanide with limited side reactions. Consequently the detoxification can be operated at a one to one molar ratio between Caro's acid and the initial WAD cyanide concentration. The free cyanide reaction occurs in one step, according to Equation 2.27.

Equation 2.27 Destruction of cyanide by peroxymonosulphuric acid

$$CN^- + H_2SO_5 \rightarrow CNO^- + H_2SO_4$$

The preferred pH of the Caro's acid process is pH 9–11. To keep the pH in this range, the generated sulphuric acid has to be neutralised by continuous addition of milk of lime or caustic soda. Unlike hydrogen peroxide it oxidises not only cyanide but also thiocyanate at a four to one molar ratio.

2.6.4 Biological treatment

In the past two decades, biological cyanide detoxification has been utilised under industrial conditions for the treatment of mine effluents. Biodegradation involves the conversion of cyanide and thiocyanate to carbon dioxide and ammonia by bacteria (Equation 2.28). It involves two separate bacterial oxidation steps. In the first step, the cyanides and thiocyanate are broken down

to ammonia and carbonate. The liberated free metal ions are subsequently adsorbed and/or precipitated into the biofilm (Smith and Mudder, 1991).

Equation 2.28 Biodegradation of metal cyanides and thiocyanate

$$M(CN)_4^{2-} + 8\ H_2O + 2\ O_2 \rightarrow M^{2+}\text{-biofilm} + 4\ HCO_3^- + 4\ NH_3$$
$$SCN^- + 2\ H_2O + {}^5/_2\ O_2 + 2\ e^- \rightarrow SO_4^{2-} + HCO_3^- + NH_3$$

In the second step, ammonia is converted to nitrate through conventional nitrification.

Equation 2.29 Nitrification of ammonia

$$NH_4^+ + {}^3/_2\ O_2 \rightarrow NO_2^- + 2\ H^+ + H_2O$$
$$NO_2^- + {}^1/_2\ O_2 \rightarrow NO_3^-$$

These reactions are often referred to as atmospheric oxidation reactions that destroy free and WAD cyanide but not SAD cyanide.

Cyanide degrading bacteria typically belong to the *Pseudomonas* genus. They use cyanide and thiocyanate as nitrogen and carbon sources but also require phosphorus as a nutrient, which can be added in the form of phosphoric acid.

2.7 PROJECT MOTIVATION

In 2004, Mintek recognised the gold mining industry's need for an online free and WAD cyanide measurement device. Gold mining companies were fast becoming signatories of the International Cyanide Management Code which requires the online measurement of WAD cyanide. Local and national regulations enforcing stricter cyanide controls were putting pressure on operations to measure both free and WAD cyanide within the plant as well as at discharge. At this time no online instrument capable of measuring both free and WAD cyanide was commercially available. Shortly after development commenced other online instruments that measured WAD cyanide only, using the picric acid method became available.

The goal of the initial stages of development was to find and validate a WAD cyanide analysis technique that could be combined with free cyanide measurement by amperometry. Summarising

the various reviews of standard methods and methodologies available for the determination of cyanides, as discussed in Section 2.3, WAD cyanide may be measured by manual distillation, or ligand exchange with amperometric or colorimetric finish (picric acid method). According to the ICMI; the preferred laboratory technique for WAD cyanide determination is manual distillation (buffering to pH 4.5 and refluxing for an hour). However, this method is most suitable for laboratory use, requiring the skills of a technician and an analysis time too long for online measurement. Micro-distillation relies on accurate dilution to very low concentrations, less than 0.200 ppm, which would require high precision pumps and thin tubing. Of the methods recommended for WAD cyanide analysis only two seemed appropriate for a robust, online device, the picric acid method and a ligand displacement method with amperometric finish. The picric acid method requires the time consuming preparation of reagents, containing potentially explosive ingredients. Given the strict safety regulations of gold plants and wariness of hazardous substances it would be preferable to avoid the use of potentially explosive reagents. Also, no associated standard test method, (ASTM, ISO or EPA) exists using this generic methodology, so likely interferences have not been defined. Colorimetric techniques are susceptible to interferences from turbidity. So, the ligand displacement method with amperometric finish was considered for validation. Ultimately, the following key objective and subsidiary aims and objectives were to be achieved.

2.7.1 Key Objective

Develop an online WAD cyanide analysis instrument, based on ligand exchange and amperometric finish, with an initial accuracy and precision comparable to laboratory techniques, and an on-going accuracy of ±10% for online analysis of actual gold plant filtrate under industrial conditions.

2.7.1.1 Aims

- The instrument's WAD cyanide reading should be suitable for environmental monitoring with a measurable WAD cyanide concentration range of 0.5-100 ppm, (applicable to ICMI environmental limits of 0.5 and 50 ppm for effluent and tailing storage facilities).
- Due to the increase in gold price and scarcity of simple, gold oxide ores, the instrument should be applicable to complex and refractory ores.
- The instrument should be suitable for cyanide destruction control and therefore should be compatible with the most common destruction oxidants.

2.7.1.2 Objectives

Laboratory development and validation:

- Select an appropriate ligand exchange reagent and optimise the WAD cyanide analysis technique (ligand exchange with amperometric finish) in the Cynoprobe.
- Determine instrument's initial and on-going precision and recovery for WAD cyanide determination using pure and combination metal cyanide standards.
- Test and if necessary remedy interferences from copper and sulphur species, as well as flotation reagents such as xanthate.
- Validate the Cynoprobe measurement in the presence of the most common destruction oxidants.

Industrial validation and implementation:

- Validate WAD cyanide measurement on gold plants treating simple and complex ore types by comparing Cynoprobe results to laboratory analyses such as SFIA micro-distillation with colorimetric finish, picric acid method and laboratory distillation.
- Generate data showing the Cynoprobe's WAD cyanide reading used for cyanide destruction control.
- Produce plant data for the Cynoprobe's WAD cyanide reading used for environmental monitoring.

CHAPTER THREE

Materials and methods

3.1 PREPARATION OF SOLUTIONS

3.1.1 Sodium cyanide solutions

A standard cyanide stock solution was prepared in the laboratory from analytical grade NaCN salt with an assay of 99% in deionised water adjusted to pH 12 with 10 M NaOH solution. All sodium cyanide solutions were prepared by appropriate dilution of standard stock cyanide solution with deionised water at pH 12, unless otherwise specified.

3.1.2 Metal cyanide solutions

Metal standard stock solutions were prepared from cyanide salts either purchased from a commercial supplier or synthesised in the laboratory at Mintek. Sodium tetracyanozincate(II) salt ($Na_2[Zn(CN)_4].2H_2O$), potassium tetracyanonickelate(II) hydrate ($K_2[Ni(CN)_4].H_2O$), potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6].3H_2O$) and potassium hexacyanoferrate(III) ($K_3[Fe(CN)_6$) were purchased from Sigma Aldrich, Merck or Associated Chemical Enterprises. The tetracyanocuprate(I) salt cannot be obtained commercially and so was synthesised at Mintek using analytical grade copper cyanide (CuCN) and potassium cyanide (KCN) salts.

3.1.2.1 Preparation of potassium tetracyanocuprate(I) hydrate

This compound was prepared as illustrated by Equation 3.1 below.

Equation 3.1 Preparation of potassium tetracyanocuprate(I) hydrate salt

$$CuCN + 3\ KCN + H_2O \rightarrow K_3[Cu(CN)_4].H_2O$$

To avoid the formation of $K[Cu(CN)_2]$ a 1:1 molar excess of cyanide should be added to copper cyanide. Potassium cyanide (403.6 g, 6.198 mol, 1.1 molar excess) was dissolved, with stirring, in

100 mL of deionised water at ambient temperature, in an Erlenmeyer flask in a fume hood. Small portions of 179.2 g (2.001 mol) copper cyanide was then slowly added to this solution. The reaction is exothermic and so the temperature was monitored so as to ensure that it did not exceed 80ºC. Water was added as necessary. Once completely mixed the solution was left to cool down overnight and was gravity filtered through a Whatman No. 541 filter paper. The filtrate was evaporated to dryness in a vacuum oven at 40ºC. Finally, it was verified against calibration standards by Segmented Flow Injection Analysis (SFIA) (see Section 3.2.2), on five separate occasions. Instead of one, it was found to have two crystallisation water molecules and the masses to make up 1 L 1000 ppm WAD CN solution were adjusted accordingly (see Table 3.1).

3.1.2.2 Validation of metal cyanide salts

Every month reference standards of all metal cyanide salts are analysed by Atomic Absorption Spectroscopy (AAS) and SFIA, to determine their purity. A series of 100 mL solutions are prepared containing theoretical 5 ppm metal and 1000 ppm total cyanide. The dissociated metal value (±10%) and the total cyanide concentration (±5%) are then determined by AAS and SFIA, respectively. The actual metal and cyanide concentrations are then compared to the theoretical values to determine the percent purity of the salt. The masses of metal cyanide salts needed to prepare 1000 ppm WAD CN were adjusted accordingly. For example, the potassium tetracyanocuprate(I) salt was expected to have one water of crystallisation but its purity of 92.6% suggested that it rather has two. Similarly, over-recoveries for the potassium tetracyanonickelate(II) and sodium tetracyanozincate(II) salts suggested zero and one water of crystallisation, respectively.

Table 3.1 Mass of metal cyanide salt (Mintek reference material) required to make up 100 mL 1000 ppm CN pure metal solutions

Metal cyanide salt	Theoretical mass (g)	Purity
$K_2[Cu(CN)_4].H_2O$	0.2535	92.6%
$K_2[Ni(CN)_4]\ H_2O$	0.2488	111.8%
$Na_2[Zn(CN)_4].2H_2O$	0.2417	112.1%
$K_4[Fe(CN)_6].3H_2O$	0.2706	99.0%
$K_3[Fe(CN)_6]$	0.2109	99.0%

3.1.2.3 Pure metal stock solutions

1000 ppm CN pure metal cyanide standards were made up with adjusted masses of metal cyanide salts, according to Table 3.2 using deionised water at pH 12.

Table 3.2 Mass of metal cyanide salt (Mintek reference material) required to make up 1 L 1000 ppm CN pure metal solutions

Metal cyanide salt	Actual mass (g)
$K_2[Cu(CN)_4].2H_2O$	2.738 g
$K_2[Ni(CN)_4].H_2O$	2.161 g
$Na_2[Zn(CN)_4].2H_2O$	2.156 g
AgCN and NaCN	2.575 g and 0.942 g
$K_4[Fe(CN)_6].3H_2O$	2.733 g
$K_3[Fe(CN)_6]$	2.130 g

The concentration of all solutions was cross-checked by SFIA. Optimisation experiments were performed using copper, nickel and zinc standard solutions, since these are the most common WAD metals encountered in gold plant solutions. However, analysis of silver cyanide solution was included in the recovery experiments to test the LEX reagent's ability to liberate cyanide from silver. Recovery of cyanide from ferric and ferrous cyanide with the LEX reagent was also tested.

3.1.2.4 Combination metal stock solution

A combination metal WAD cyanide solution that is most representative of plant filtrate, considering majority application, was prepared to consist of 40% free cyanide, 40% cyanide bound to copper and 20% cyanide bound to nickel. This was prepared from the cyanide salts according to Table 3.3 with deionised water at pH 12.

Table 3.3 Mass of metal cyanide salts required to make up 1 L 1000 ppm CN combination metal solution

Metal cyanide salt	Mass (g)
NaCN	0.7572 g
$K_2[Cu(CN)_4]$	1.0291 g
$K_2[Ni(CN)_4]$	0.4503 g

3.1.2.5 Copper cyanide solutions with varying copper to cyanide ratios

Pure copper cyanide solutions, with excess and starved of free cyanide with copper cyanide ratios 1:7 and 1:2.5 were prepared in an attempt to obtain $[Cu(CN)_4]^{3-}$ and $[Cu(CN)_2]^-$, respectively, in addition to $[Cu(CN)_3]^{3-}$. The copper content of both solutions was 63 ppm (1 mM/L). The solutions were prepared from analytical grade CuCN and NaCN in deionised water at pH 12 and 9.31 according to Table 3.4 below.

Table 3.4 Mass of metal cyanide salts required to make up 1 L copper cyanide solutions with excess and starved of free cyanide (63 ppm (1 mmol) Cu)

Cu:CN	Metal salt mass (g)	
	NaCN	CuCN
1:7	0.288	0.0905
1:2.5	0.068	0.0905

3.1.3 Sulphur-containing solutions

Solutions of sulphur species including thiocyanate, sulphide and thiosulfate ions, polythionates and polysulfides were prepared by dissolving the salts in deionised water. The following table shows the masses of analytical grade salts used to prepare 1000 ppm of the required species.

Table 3.5 Mass of sulphur salts required to make up 1 L 1000 ppm

Sulphur salt	Mass (g)
Sodium sulphide - $Na_2S.9H_2O$	7.490 g
Potassium thiocyanate – KSCN	1.673 g
Sodium thiosulphate - $Na_2S_2O_3$	1.410 g
Sodium sulphite - Na_2SO_3	1.574 g
Sodium dithionate dehydrate - $Na_2S_2O_6.2H_2O$	1.512 g
Potassium tetrathionate - $K_2S_4O_6$	1.349 g
Sodium pyrosulphate - $Na_2S_2O_7$	1.261 g
Sodium sulphate - Na_2SO_4	1.148 g

3.1.4 Reagents for removal of interference

3.1.4.1 Lead acetate

A slight excess of lead acetate with a 1.1:1 molar ratio between lead acetate and 10 ppm sulphide per 100 mL sample in the Cynoprobe cell was prepared. 5500 ppm lead acetate was prepared from reagent grade, 95% lead acetate trihydrate ($Pb(CH_3COO)_2.3H_2O$) with deionised water at a slightly alkaline pH, according to the pH of the filtrate to be analysed (at higher pH's lead hydroxide will form).

3.1.4.2 Sodium thiosulphate

1000 ppm thiosulphate solution was prepared for the removal of negative interference from oxidants such as hydrogen peroxide and ozone. 1.410 g of 99% $Na_2S_2O_3$ salt was added to 1 L deionised water to form a naturally alkaline solution. The solution was freshly prepared before each

experiment but should be replaced every month when used on site.

3.2 ANALYSIS OF CYANIDE SOLUTIONS

Sodium cyanide solutions for the calibration of the Cynoprobe were analysed for free cyanide by potentiometric silver nitrate titration. WAD cyanide standard solutions prepared in the laboratory were analysed at Mintek by SFIA with ISO 17025 accreditation. Online WAD cyanide analysis data was validated by a range of laboratory techniques, SFIA, gas diffusion ligand exchange with amperometric finish, manual distillation (ICMI recommended technique) and the picric acid method.

3.2.1 Potentiometric Silver Nitrate Titration

Potentiometric titration was performed by adding silver nitrate solution of appropriate concentration to the cyanide liquor in small quantities and measuring the potential, in millivolts (mV), after a suitable stabilisation period. A plot was then generated of volume of titrant versus potential. The end-point was determined from the inflection point.

3.2.1.1 Analysis procedure

Potentiometric titration was used to analyse free cyanide with concentrations ranging from 2 to 2000 ppm. Titrations were performed using a 0.010 M silver nitrate solution connected to a Metrohm 808 Titrando autotitrator controlled by the Tiamo 2.0 software fitted with a combined platinum indicator and glass reference electrode. The volume of analyte was varied according to the expected analyte cyanide concentration.

3.2.1.2 Sample analysis replication

Cynoprobe calibration standards were analysed in triplicate and the average concentration was used to determine calibration constants.

3.2.2 SKALAR SAN^{++} Segmented Flow Injection Analyser

WAD cyanide, Total cyanide and thiocyanate were determined in the SKALAR SAN^{++} Segmented Flow Injection Analysis instrument in the Mintek Cyanide Centre.

3.2.2.1 Analysis procedure

The procedure for analysis consists of separation by micro-distillation with a colorimetric finish. It is an analogue to ASTM D-4374 – 93 or SANS/ISO 14403-2002. The sample was firstly introduced into a continuous flow stream using an auto sampler. The stream was buffered to a pH value of 4.5 using an acetate buffer and the sample together with the acetate buffer was passed through a distillation system where the cyanide, in the form of hydrogen cyanide, was separated from the matrix. The matrix was pumped to waste while the hydrogen cyanide was re-sampled and introduced into the colour formation circuit. In this circuit the hydrogen cyanide was buffered to a pH value of 5.2 and reacted with chloramine T to form cyanogen chloride. The cyanogen chloride was reacted with 1,3 dimethylbarbituric acid to form a purple dye which is detected at 600 nm. The output from the detector was linked to a computer system where the signal from the sample was compared, using the software supplied with the instrument, to that obtained for the calibration standards. In this way, the output signal from the detector was converted into a concentration value for the original sample.

3.2.2.2 Performance specifications

The Mintek Cyanide Centre SKALAR SAN^{++} Segmented Flow Injection Analyser has the following performance specifications; a lower detection limit (LDL) of 0.002 ppm (2 ppb), a quantification limit of 10 ppb for both the WAD and Total channels, dynamic range of 0.002-0.200 ppm CN and sensitivity of 0.002 ppm (2 ppb) CN.

The standard uncertainty of the analytical results, from statistical analysis of several months' data, analysing a variety of matrix constellations is calculated periodically. Based on a standard deviation of 1 sigma, [68% confidence], the uncertainty is currently 2.9% for the WAD cyanide channel and 3.1% for the Total cyanide channel. For a higher level of confidence of 95%, the uncertainty of the results is currently 5.8% for the WAD cyanide channel and 6.2% for the Total cyanide channel.

3.2.2.3 Sample analysis replication

Each real plant solution was analysed once and repeated if results were not as expected or if the calibration drift sample was not within the required limits of uncertainty.

3.2.3 O I Analytical Flow Solution® FS 3100 Automated Cyanide Analyser

The Flow Solution® FS 3100 automated cyanide analyser uses a gas diffusion ligand exchange procedure before measuring the available cyanide with a highly sensitive expanded range amperometric detector. It is used by a number of laboratories that service gold plants.

3.2.3.1 Analysis procedure

The FS 3100 analyser injects the sample into a carrier stream, where it is segmented and acidified to release hydrogen cyanide. The hydrogen cyanide passes through a hydrophobic membrane and is absorbed into a basic acceptor solution. The hydrogen cyanide enters a low-dead-volume flow-cell, where a silver working electrode measures the cyanide amperometrically. The signal generated by the detector progresses to software for interpretation and final output generation (OI Analytical, 2012).

3.2.3.2 Performance specifications

The FS 3100 has the following performance specifications; a detection limit (DL) of 0.002 ppm (2 ppb) CN, lower detection limit (LDL) of 0.0005 ppm (0.5 ppb) CN, dynamic range of 0.002-5 ppm CN and sensitivity of 0.002 ppm (2 ppb) CN (OI Analytical, 2012).

3.2.4 Laboratory distillation

The distillation method creates chemical conditions which allow the WAD cyanide to be liberated as dissolved hydrogen cyanide gas which once adsorbed into a caustic soda solution appears as free cyanide and is measured by silver nitrate titration or colorimetry.

3.2.4.1 Analysis procedure

According to ASTM or ISO/DIS distillation may be performed manually or in a specially designed unit. WAD cyanide is liberated from an acidified sample (pH 4.5-6) by reflux distillation for at least an hour. Liberated hydrogen cyanide gas is then carried in an air stream to a caustic soda solution where it is adsorbed in a much smaller volume than the original sample solution. The free cyanide concentration to be analysed is typically at least ten times higher than the original WAD cyanide concentration in the sample solution. The free cyanide concentration in the distillation product sample is then determined using silver nitrate titration or colorimetric finishes.

3.2.4.2 Performance specifications

According to standard test methods this technique has a detection limit of 0.05 ppm.

3.2.5 Picric Acid Method

Picric acid (trinitrophenol) can be used in a colorimetric procedure to determine the concentration of WAD cyanide, after the addition of a ligand exchange reagent. In the presence of free cyanide, picric acid is reduced to the orange coloured isopurpuric acid with the colour intensity directly proportional to the concentration of free cyanide originally present in the sample.

3.2.5.1 Analysis procedure

No associated standard method exists for the picric acid method. The procedure for analysis is firstly to liberate WAD cyanide using diethylenetriaminepenta-acetic acid (DTPA) and thereafter add picric acid which reacts with free cyanide to form the orange coloured isopurpuric acid which can be measured colorimetrically. Two reagents are required for addition to the cyanide sample; a picric acid reagent consisting of 40 g/L DTPA, 6 g/L picric acid, 14 g/L sodium borate and 8 g/L sodium carbonate adjusted to pH 8.7 with sodium hydroxide and a nickel reagent consisting of 0.44 g/L nickel sulphate and 2 g/L sodium chloride. 10 mL of the sample, 1 mL nickel solution, 25 mL picric acid solution and 30 mL deionised water are mixed in a 100 mL volumetric flask. The sample is then heated in a water bath for 20 minutes. After it has cooled to room temperature it is diluted to 100 mL using deionised water. Finally, the absorbance of the solution is measured at 520 nm.

The pH of the sample should be checked and carefully controlled as the intensity of the colour development varies outside the pH range of 9.0-9.5. Safety precautions associated with this methodology include the careful handling of picric acid which is explosive in its dry form.

3.2.5.2 Performance specifications

The picric acid method provides reliable results for WAD cyanide concentrations ranging between 0.02 ppm and 3 ppm. The measurement of higher concentrations relies on dilution.

3.2.6 Cynoprobe

The Mintek Cynoprobe was used to measure free cyanide by amperometry. In the presence of an applied potential, a limiting current is established which is proportional to the concentration of the analyte. The WAD cyanide measurement that was validated was based on ligand exchange with amperometric finish.

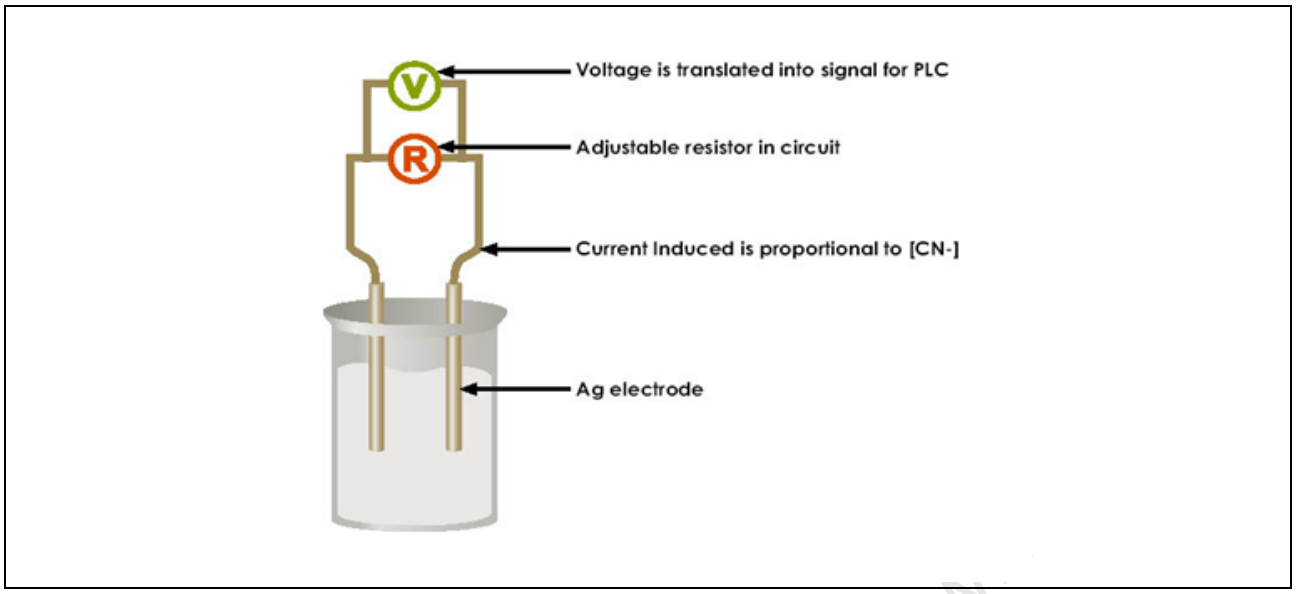
3.2.6.1 Analysis procedure

See Section 2.5.2 for principles behind the Cynoprobe's free cyanide measurement technique. For confidentiality reasons, complete details of the Cynoprobe's operation are beyond the scope of this thesis. Information required by operators is included in the User Manual that is supplied to purchasers of the instrument.

3.2.6.1.1 Cynoprobe calibration

The Cynoprobe was calibrated with standards prepared from analytical grade NaCN and deionised water at pH 12, and titrated by potentiometric titration. Each sample was analysed at least four times and the PLC 'counts' recorded. The 'counts' is the PLC's interpretation of the current induced by the reaction of cyanide with the silver electrode. As shown in **Error! Reference source not found.**, the current from the oxidation of silver to dicyanoargentate(I) is converted to voltage by placing a resistor in the circuit (potentiostat board) which is then translated into 'counts' by the PLC. The 'counts' range between -20 000 and 20 000 and are proportional to the cyanide concentration.

Figure 3.1 A simplified diagram of the electronic circuit of the Cynoprobe



Calibration constants were obtained from a best fit equation to a linear plot of actual concentration versus 'counts'. These constants were programmed into the instrument software and used to determine the actual concentration of samples analysed.

The calibration relied on the following variables that had to be set in the hardware or software.

- Current sensing resistance
- Filtrate temperature set-point
- Measurement time (60 s unless otherwise specified)
- Time to mix ligand exchange reagent in cell (20 s)

3.2.6.1.2 Cynoprobe voltammograms

The Cynoprobe uses amperometry to measure the concentration of cyanide ions in solution. Amperometry is a subsidiary of voltammetry. Voltammetry is the study of current as a function of applied potential, whereas amperometry is the determination of the resulting current at a fixed potential. Voltammograms illustrate the relationship between applied potential and the current resulting from the oxidation of the analyte at the anode (Atkins, 1998).

Voltammograms were plotted by varying the applied potential via the potentiostat board and recording the resulting current due to oxidation of the cyanide. The Cynoprobe potentiostat board is the interface between the PLC and voltammetric cell and is used to control the voltage between the

working electrode (Ag) and reference electrode (Ag/AgCl) to a user-defined set-point. For a chosen resistance, the voltammograms of silver cyanide and other silver compounds were plotted by varying the voltage set-point and recording the resulting steady state current in the silver electrode after 60 seconds. This was achieved indirectly by measuring the voltage going to the PLC (see **Error! Reference source not found.**). A Fluke 87 IV multimeter in DC mode was connected in parallel, across the ground and output of the potentiostat board.

Current density of the working electrode was calculated according to **Error! Reference source not found.**.

Equation 3.2 Calculation of current density on working electrode

$$\text{Current density (mA/cm}^2\text{)} = \frac{\text{Voltage (V) x 1000}}{\text{CSR (}\Omega\text{) x Multiplier x Gain x SA (cm}^2\text{)}}$$

CSR = potentiostat board current sensing resistor resistance; Multiplier = autoranging multiplier (if enabled, 1, 4, 16, 64); Gain = 5 (output amplifier); SA = surface area of working electrode.

Silver cyanide voltammograms were plotted in order to determine at what potentials cyanide may be measured, as well as the behaviour of interfering species such as the LEX reagent, thiosulphate, and chloride, at various applied potentials. A copper electrode was also used in order to compare the stability of copper and cyanide species.

3.2.6.2 Cynoprobe Instrumentation

Since the work presented in this thesis has been completed over several years, the Cynoprobe has been under continual development and there have been many hardware and software changes. These changes were incorporated into version upgrades, the full details of which are beyond the scope of this thesis. The main differences between each version, that are of relevance to the work presented in this thesis, are listed below.

3.2.6.2.1 Cynoprobe v 1.0

Cynoprobe v1.0 was essentially a one stream, free cyanide analysis instrument utilising potentiostat board v1.0. Since it did not include temperature control, it relied on calibration at relevant temperatures. This instrument was not utilised for any work presented in this thesis.

3.2.6.2.2 Cynoprobe v 2.0

Cynoprobe v2.0 included functionality to measure the free and WAD cyanide concentration and pH of two streams. It included temperature control to a user defined set-point and utilised potentiostat board v1.0 or v2.0. The working silver, counter and reference electrodes were arranged in a cylindrical, glass amperometric cell.

3.2.6.2.3 Cynoprobe v 3.0

Cynoprobe v3.0 included functionality to measure the free and WAD cyanide concentration and pH of three streams, utilising potentiostat board v2.0. The amperometric cell was redesigned to increase accuracy especially at high concentrations. It was redesigned with symmetrical cell geometry to minimise the effect of the voltage drop due to the resistance of the solution and variable currents at the silver electrode. The working silver electrode was either cylindrical or hemispherical in shape for concentrations less than and greater than 500 ppm, respectively (Barker, 2007).

3.2.6.3 Sample analysis replication

Each calibration solution was analysed at least four times. Validation experiments were performed by analysing each sample at least seven times. Repeatability and accuracy experiments were performed by analysing each sample at least ten times. Online sample analysis was performed once.

3.2.6.4 Accuracy, precision and repeatability calculations

The instrument's initial precision and recovery of WAD cyanide was calculated using the equations below. Percent recovery was calculated using Equation 3.3 from analysing samples seven times. The standard deviation of the percent recovery was computed according to Equation 3.4. Relative standard deviation was calculated according to Equation 3.5.

The precision and repeatability was determined by calculating the relative standard deviation from the ten results for each standard

Equation 3.3 Calculation of average percent recovery

$$X\ (\%) = \frac{Average\ concentration\ (ppm)}{Actual\ concentration\ (ppm)}\ x\ 100$$

X = average percent recovery.

Equation 3.4 Calculation of standard deviation of percent recovery

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

s = standard deviation; x = percent recovery in each sample; n = number of samples.

Equation 3.5 Calculation of relative standard deviation

$$RSD\ (\%) = \frac{s}{Average\ concentration}\ x\ 100$$

RSD = Relative Standard Deviation; s = standard deviation.

3.2.6.5 Limits of detection and quantification

According to Harvey, 2000, the International Union of Pure and Applied Chemistry (IUPAC) defines the detection limit (DL) according to Equation 3.6 as the signal for a reagent blank plus the standard deviation (σ) for the reagent blank's signal multiplied by a factor accounting for the desired confidence level, typically 3, which corresponds to a significance level of alpha = 0.00135 and confidence level of 99.9%.

Equation 3.6 Calculation of detection limit according to IUPAC

$$DL = S_{reag} + z\ \sigma_{reag},\ z = 3$$

$_{reag}$ = signal for a reagent blank, σ_{reag} = standard deviation for reagent blank

The American Chemical Society's Committee on Environmental Analytical Chemistry recommends the quantification limit (QL) or lower quantification limit (LQL), which is defined according to Equation 3.7 as the lowest concentration at which the analyte can be quantified. This equation was used to calculate the quantification limit at high resistances (10 000 Ω for potentiostat board v1.0, 4020 Ω and 1214 Ω for potentiostat board v2.0).

Equation 3.7 Calculation of quantification limit according to American Chemical Society's Committee on Environmental Analytical Chemistry

$$QL = S_{reag} + 10\,\sigma_{reag}$$

$_{reag}$ = signal for a reagent blank, σ_{reag} = standard deviation for reagent blank

The quantification limit is also sometimes defined as three times the detection limit (ICMI, 2011). The quantification limit may be equivalent to or greater than the detection limit. The above statistical interpretations were applied to all the Cynoprobe data but were found to be inadequate. Only considering the blank sample in determining the detection limit did not make sense and produced obviously incorrect limits in some cases. The Cynoprobe can measure various concentration ranges depending on the resistance. At lower resistances high concentration ranges can be measured. It made sense to consider the signal and standard deviation of the lowest measurable concentration in determining the quantification limit at these resistances. Hence other approaches for defining the detection limit and the quantification limit were considered. The definitions that included the lowest, measurable concentration, according to Equation 3.8 were more appropriate for the Cynoprobe (ABSCIEX Technology, 2011). The limit of blank (LoB) is defined according to Equation 3.8 (b) and should also be considered in the detection limit. The quantification limit (QL) was calculated according to Equation 3.8 (c), considering the signal and standard deviation from the lowest analysable concentration and a confidence level of 95%.

Equation 3.8 Calculation of quantification limit according ABSCIEX Technology (2011)

$$DL = LoB + 1.645\,(SD_{low\ conc\ sample}) \quad (a)$$

$$LoB = mean_{blank} + 1.645\,(SD_{blank}) \quad (b)$$

$$QL = S_{low\ conc\ sample} + 1.645\,(SD_{low\ conc\ sample}) \quad (c)$$

SD_{blank} = standard deviation for reagent blank, $SD_{low\ conc\ sample}$ = standard deviation for low concentration sample; $S_{low\ conc\ sample}$ = signal for low concentration sample.

In the case of the Cynoprobe these limits were calculated for sodium cyanide solutions that were analysed at least ten times at various resistances for potentiostat board v1.0 and 2.0. A blank sample analysis was performed with tap water at pH 12 (0.01 M NaOH).

3.3 CHEMICAL MODELLING OF CYANIDE SYSTEMS

The meaningful analysis of cyanide-containing systems hinges upon an understanding of the

chemical species present in such a system. This can be obtained from chemical equilibrium modelling of each system for which a meaningful analysis is required. Stability constants for the major metal cyanide species are relatively well known and there are several thermodynamic modelling programs available such as Visual MINTEQ, OLI, STABCAL and JESS that include a database of thermodynamic properties for a range of chemical species. The theoretical speciation of the laboratory prepared metal cyanide solutions was determined using Visual MINTEQ as well as a Mintek Cyanide Centre speciation spread-sheet. Visual MINTEQ is one of the most commonly used chemical equilibrium software application among researchers publishing in Elsevier journals. It is a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria, and sorption for natural waters. The code was originally built on USEPA's MINTEQA2 software; it now runs on most Windows platforms and relies on .NET Framework (Visual MINTEQ, 2010). The Mintek Cyanide Centre speciation spread-sheet is a proprietary chemical modelling program prepared in excel. It requires inputs such as pH, Eh, metal and cyanide concentration in order to determine the expected cyanide species in solution. Figure B.1 is a screen shot of the predicted cyanide speciation of a gold leach liquor based on WAD and Total cyanide analysis by SFIA performed in the Mintek Cyanide Centre. All Tables in Appendix B show the theoretical speciation of cyanide systems as predicted by Visual MINTEQ and the Mintek Cyanide Centre speciation spread-sheet.

3.4 CYANIDE DESTRUCTION EXPERIMENTS

Experiments were performed in Mintek's laboratories in order to assess the Cynoprobe's ability to monitor the destruction of cyanide in the presence of the most common oxidants. For WAD cyanide measurement 2 mL 20% LEX reagent was added to the Cynoprobe's amperometric cell. 100 ppm WAD cyanide solutions were prepared from a 1000 ppm combination metal (40% free cyanide, 40% copper and 20% nickel) stock solution.

3.4.1 Sodium meta-bisulphite and oxygen

3.4.1.1 Blank solutions

1.462 g sodium meta-bisulphite was added to 2 L tap water at pH 12 with and without LEX reagent and the Cynoprobe amperometric response was recorded over seven to ten readings.

3.4.1.2 WAD cyanide destruction

A two-fold excess of sodium meta-bisulphite was added to 100 ppm WAD cyanide solutions, whilst purging with oxygen. 1.462 g sodium meta-bisulphite was added to 2 L of 100 ppm WAD cyanide solution in the presence of oxygen and the destruction was monitored over an hour. The copper catalyst was omitted so as to reduce the reaction speed and enable the Cynoprobe to track the destruction. 2 mL 20% LEX reagent were added to the Cynoprobe cell during a WAD cyanide measurement. The Cynoprobe's WAD cyanide measurement was validated by the SFIA technique performed at Mintek's ISO 17025 accredited laboratories. The frequency of the Cynoprobe's online measurements was ~8 minutes, while that of SFIA varied between 5 and 15 minutes. The pH and temperature of the reaction vessel was monitored.

3.4.2 Hydrogen peroxide

3.4.2.1 Blank solutions

1.571 mL of 30% hydrogen peroxide was added to 2 L tap water at pH 12 with and without LEX reagent. 2000 ppm cyanate was also prepared in tap water from 96% sodium cyanate. Seven to ten readings were taken with the Cynoprobe.

3.4.2.2 WAD cyanide destruction

A two-fold excess of hydrogen peroxide was added to 100 ppm WAD cyanide solutions, in the presence of 20 ppm copper. 0.039 g of 98% cupric sulphate pentahydrate ($Cu(SO_4).5H_2O$) and 1.57 mL 30% hydrogen peroxide was added to 2 L of 100 ppm WAD cyanide solution. The destruction was monitored over an hour and a half by the Cynoprobe and SFIA. 0.5 mL of slightly alkaline, 1000 ppm thiosulphate solution, prepared from 99% $Na_2S_2O_3$, was added to the Cynoprobe cell to obtain a concentration of approximately 5 ppm, in the cell prior to measurement. 2 mL 20% LEX reagent were added to the Cynoprobe cell for WAD cyanide measurement. The Cynoprobe's WAD cyanide measurements were validated by the SFIA technique performed at Mintek's ISO 17025 accredited laboratories. The frequency of the Cynoprobe's online measurements was ~7 minutes, while that of SFIA varied between 5 and 15 minutes. The pH and temperature of the reaction vessel was monitored.

3.4.3 Caro's acid

3.4.3.1 Synthesis

Caro's acid was prepared in the laboratory by mixing 98% sulphuric acid and 50% hydrogen peroxide in a 3:1 molar ratio (263 g of 98% H_2SO_4 and 59.7 g of 50% H_2O_2). A dropping funnel was used to slowly add the hydrogen peroxide to the sulphuric acid in a round bottomed flask whilst stirring rapidly and cooling with ice. The temperature of the reaction mixture was not permitted to exceed 15 °C.

3.4.3.2 Blank solutions

0.4 mL of freshly synthesised Caro's acid was added to 2 L tap water at pH 12 with and without LEX reagent. Seven to ten readings were taken with the Cynoprobe.

3.4.3.3 WAD cyanide destruction

A molar equivalent of freshly synthesised Caro's acid was added to 100 ppm WAD cyanide solution. 0.4 mL Caro's acid was added to 2 L of 100 ppm WAD cyanide solution. The pH was controlled to ten by the manual addition of 10 M sodium hydroxide. The destruction was monitored over an hour and a half by the Cynoprobe and SFIA. The frequency of the Cynoprobe's online measurements was ~10 minutes, while that of SFIA varied between 5 and 15 minutes.

CHAPTER FOUR

Development of an online free and WAD cyanide measurement device

4.0 WAD CYANIDE MEASUREMENT TECHNIQUE

The goal of the initial stages of development was to find and validate a WAD cyanide analysis technique that could preferably be used in conjunction with Mintek's free cyanide analyser, the Cynoprobe. The idea was to develop an instrument that could measure both free and WAD cyanide concentrations frequently online.

Standard test methods and methodologies for WAD cyanide analysis consist of at least two steps; liberation of cyanide bound to metals followed by a free cyanide analysis finish. Cyanide liberation may either be achieved by reflux distillation at a pH of approximately 4.5 or by using a ligand exchange reagent. Free cyanide may be determined amperometrically, colorimetrically, by titration, or by selective ion electrode. Separation of cyanide from the matrix by either distillation or the use of a membrane improves accuracy, particularly at low concentrations. A one hour distillation in the presence of a weak acid, such as an acetate buffer is required for decomposition of WAD cyanide (ISO/DIS 6703/2, DIN 38405, ASTM D-2036, US-EPA 9010, APHA 4500, ASTM D-4374). This is a time-consuming technique and requires fragile apparatus. The ligand exchange technique however is much simpler and so seemed more appropriate for a robust, online device (US-EPA OIA-1677, ASTM D-6888-4). The picric acid method is a well-known colorimetric procedure for the analysis of WAD cyanide. Its accuracy depends on colour development which requires close pH control between 9.0 and 9.5 and consistent contact times. It also requires the time consuming preparation of reagents, containing potentially explosive ingredients and no associated standard test method, (ASTM, ISO or EPA) exists using this generic methodology (Iamarino, 1989). Ligand exchange followed by amperometry seemed most suitable for implementation in Mintek's existing free cyanide analyser, the Cynoprobe.

A ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. The cyanide ion is a monodentate ligand since it binds to the metal cation via one donor site. Typically, the cyanide ion binds through the carbon atom, forming a strong covalent bond with the metal but it can also bridge metals atoms, where either both atoms are bound to carbon or one to

carbon and one to nitrogen. Ligands that bind via more than one atom are often termed chelating. The formation of chelating complexes by polydentate ligands is favoured over complexes derived from monodentate ligands because of enhanced stability. This enhanced stability is mostly attributed to the effects of entropy, as one polydentate ligand displaces many ligands. The more rigid and the higher its denticity, the more inert will be the macrocyclic complex. Chelators are usually organic compounds that bond with the metal cation via one or more nitrogen, phosphorous or sulphur atom, via donation of electron couple. The term chelator is derived from the Greek word 'chelè', meaning claw; which appropriately likens the arrangement of the ligands around the central atom to the claws of a lobster (Shriver *et al.* 1994). Thus, a chelating agent may be used to liberate WAD cyanide during a ligand exchange reaction according to Equation 4.1.

Equation 4.1 Ligand exchange reaction

$$Metal(CN)_X + y\ Ligand \rightleftharpoons Metal(Ligand)_y + x\ CN^-$$

An exception occurs in the case of copper. Copper cyanide complexes are formed with Cu^{1+} (see Table 2.1), whereas copper chelating complexes are formed with Cu^{2+} (see Section's 4.1.2 and 4.1.3). Therefore the displacement of cyanide from copper by a chelating agent is likely to also involve a redox reaction. The mechanism could not be found in literature; however the ligand exchange reaction could possibly also involve oxidation according to Equation 4.2. This reaction is likely to occur due to the high stability of the Cu^{2+} complex with organic ligand but still requires an oxidant such as dissolved oxygen. There should therefore be sufficient oxygen present in a leach liquor before the reaction will occur. Higher DO levels will increase the efficiency of the reaction according to Le Chatelier's principle.

Equation 4.2 Oxidation of copper cyanide with ligand exchange

$$[Cu(CN)_4]^{3-} + {}^1/_2\,O_2 + Ligand + H_2O = Cu(Ligand) + 4\ CN^- + 2\ OH^-$$

Since large organic ligand exchange reagents are principally a mixture of a number of organic compounds including linear, branched and cyclic products the metal (M)-ligand (L) stoichiometry is not certain. It is likely to be 1:1 but may also be 1:2 or 1:3 in some cases.

4.1 LIGAND EXCHANGE REAGENT SELECTION

4.1.1 Metal selectivity

An appropriate ligand exchange reagent was selected with specific and potent enough chelating ability to bind with the WAD cyanide metals that are most predominant in gold mining solutions.

In general, native gold contains some copper, iron and silver, and only traces of nickel, zinc, cadmium, lead, mercury, cobalt, platinum and palladium (Lorösch, 2001). Cations that contribute to WAD cyanide include copper, nickel, silver, zinc, cadmium, lead and mercury. Many gold ores and concentrates contain minor amounts of soluble mercury and lead (Marsden and House, 2006). The Mintek Cyanide Centre database of diagnostic leaches shows that lead concentrations are typically less than 10 ppm. Cadmium is also seldom present in leach filtrate. Only refractory ore samples analysed at Mintek have shown concentrations not more than 1 ppm. Zinc minerals occur infrequently and usually in small quantities in gold ores (Marsden and House, 2006). However, when present, zinc concentrations can be as high as 150 ppm in samples associated with refractory ore from all over Africa. Nickel is also typically found in trace amounts, in concentrations <10 ppm in gold leach filtrate and <2 ppm in the residue. However, it is more widely associated with various ore types (Mintek Cyanide Centre database).

Silver is known to occur with gold in economically significant quantities and is often recovered together with gold. In such cases elevated cyanide concentrations, which can be as high as 10 000 ppm are required to obtain reasonable silver and gold extractions (Marsden and House, 2006). In silver recovery plants, particularly in central and South America where the world's largest and richest epithermal silver deposits are found; the leach may contain high concentrations of silver, up to 1000 ppm (Hancock and Skinner, 2000). However, experience has shown that silver tends to either be present in high concentrations or hardly at all, <2 ppm (Mintek Cyanide Centre database, personnel plant experience).

Copper is most commonly associated with gold and readily dissolves in an alkaline cyanide medium. Copper concentrations in the gold leach vary, up to 140 ppm. They may be 600-800 ppm or higher in processes that also recover copper. Residue concentrations from ‘clean’ ore are typically ~10 ppm. According to the Mintek Cyanide Centre database WAD cyanide is most often attributed to the presence of copper.

The ligand exchange reagent should therefore be most selective for copper, followed by nickel, zinc, silver, cadmium, lead and mercury cations. The reagent should show limited ability to bind with SAD cyanide metals; iron and cobalt.

4.1.2 Organic chelating agents

Typical organic ligands that form stable complexes with base metals were considered. It was highly unlikely that a suitable inorganic ligand would be found since the cyanide ion is known to be one of the strongest inorganic ligands (Shriver *et al.* 1994). Ethyleneamines and polycarboxylic acids are often used as chelating agents for most di- or polyvalent metals, in industry. Being the simplest ethylene amine, ethylenediamine (EDA) is the building block of other polyethylene amines such as diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and pentaethylenehexamine (PEHA), up to polyethylene amine. Ethyleneamines are liquids consisting of linear, branched, and cyclic molecules. Related derivatives of ethylenediamine include tetramethylethylenediamine (TMEDA), and tetraethylethylenediamine (TEEDA) (Huntsman International, 2001-2012 and Dow Chemical Company, 1995-2012). The most well-known commercial family of chelating agents is ethylenediamine tetraacetic acid (EDTA) and its various sodium salts, made from EDA. Other well-known polyamino carboxylic acids are diethylenetriaminepenta-acetic acid (DTPA), and cyclohexylenedi nitrilo-tetraacetic acid (CDTA). 1,4,7,10-tetraazacyclododecane-N,N',N",N"-tetraacetic acid (DOTA) is a relatively new complexing agent which is said to form more stable complexes with transition and lanthanide metals than the corresponding DTPA complexes (Byegard *et al.* 1998). Chelating agents known to be selective for nickel, zinc and silver were also considered. Dimethylglyoxime ($dmgH_2$) is used as a chelating agent for the gravimetric analysis of nickel (Tschugaeff, 1905). Di(ethylhexyl)phosphoric acid (DEHPA) is a highly effective extractant used in solvent extraction to recover vanadium, beryllium, yttrium, cobalt, zinc, rare earths and other valuable metals (Sato, 1989). ASTM D-6888 recommends dithizone as a ligand exchange reagent for liberation of cyanide from mercury. Dithizone is also recommended as a chelating agent for silver (Fries and Getrost, 1977). It is a sulphur containing organic compound known to form complexes with lead and mercury (Poljanski, 1986).

4.1.3 Comparison of stability constants and physical properties

The stability constants of various chelating complexes that are formed with WAD and SAD cyanide metals were compared in the process of selecting the most suitable reagent to recover WAD cyanide. These are available in various stability constant text books such as Sillen and Martell (1971), Smith and Martell (1975), Clarke and Martell (1991) and Anderegg *et al*. (2005).

Stability constants for two or three ligands per metal ion are available for EDA, DETA, TETA and TMEDA since they are smaller molecules with shorter organic chains and fewer binding sites. Larger ethyl amines and polyamino carboxylic acids are polydentate ligands, completely surrounding the metal and forming even more stable complexes. The general order of stability according to literature and confirmed by the stability constants from various sources is EDA < DETA < TETA < TEPA < EDTA < CDTA < DTPA < DOTA (Maqsood *et al.*, 2002 and Byegard *et al*., 1998). CDTA and DTPA are known as better complexing agents than EDTA on the basis of increased basicity and co-ordination sites. DOTA forms very rigid and hence extremely stable complexes. However, even those organic ligands with high affinity for WAD metals have stability constants lower than the corresponding WAD metal cyanide complexes. Once again this highlights the strength of cyanide as an inorganic ligand and emphasises its efficacy as a lixiviant for metal extraction. However, the organic ligand exchange reagents are still effective for metal extraction when added in excess. This should be considered when optimising the volume of ligand exchange reagent used for recovery of WAD cyanide.

The first step taken in selecting the most appropriate ligand exchange (LEX) reagent was to identify those that showed the best affinity for WAD type metals (copper, nickel, silver, cadmium, lead, mercury) over SAD type metal ions (iron and cobalt). This would make it a suitable choice for universal application, ensuring that SAD cyanide is not also recovered.

Then, the physical properties of each candidate LEX reagent were considered. Since cyanidation is a hydrometallurgical process, the reagent had preferably to be soluble in or at least miscible with water. It was also necessary to be selective for WAD metal cations from pH 9.5-11. It had to be thermally stable under normal conditions and preferably exhibit a broad liquid range for application on plants where extreme temperatures are encountered in winter and summer; with a freezing point less than -40 °C and boiling point greater than 50 °C. Its vapour pressure was considered so as to ensure that it was not volatile. Its viscosity was also considered as to determine whether a diluted form was necessary. Its prepared form had to be alkaline so as to avoid the evolution of hydrogen cyanide gas upon addition to the cyanide filtrate. It also had to show limited reactivity with air and have a shelf life of at least a month in its prepared form. No serious health and safety warnings were to be associated with its use, such as being severely corrosive, flammable (flashpoint >38°C, preferably >93°C), explosive or toxic. Finally, cost and availability were considered anticipating commercial implementation. It had to be reasonably priced compared to other reagents and be readily available in bulk from international chemical suppliers such as Merck, Sigma Aldrich and Huntsman international. A LEX reagent was selected that best met all the requirements. The exact

identity of the reagent cannot be disclosed due to confidentiality constraints stipulated by Mintek.

The chosen reagent was most selective for copper, with reasonably potent chelating ability with other WAD metals such as nickel, zinc and cadmium, and a strong affinity for mercury. All ethylamines and polyamino carboxylic acids, however, show little ability to form silver chelates, with stability constants <8.7. Though this is the case, silver cyanide complexes are significantly weaker than those of copper and nickel by approximately 10 units and the difference between the stabilities of the chelated and cyanide complexes are similar to those of nickel.

4.2 OPTIMISATION OF LIGAND EXCHANGE REAGENT IN CYNOPROBE

Before the measurement of WAD cyanide could physically be incorporated into the Cynoprobe, the ligand exchange technique needed to be optimised. The WAD cyanide measurement technique by ligand exchange with amperometric finish was optimised according to:

- volume of ligand exchange reagent (considering metal concentration variability on plants based on mineralogy).
- amperometric applied potential in the presence of the ligand exchange reagent (generating voltammograms by varying the applied potential and recording current).
- contact time between ligand exchange reagent and metal cyanide solution.
- temperature (20-45 °C).

The contact time and temperature optimisation experiments were performed using copper, nickel and zinc cyanide solutions, since these metals are most common in contributing to WAD cyanide in real mining solutions. Since the Cyanide Code WAD cyanide concentration limits are 0.5 and 50 ppm WAD CN for the effluent and tailings storage facility and residual WAD cyanide leach filtrate solutions are not expected to have concentrations more than 100 ppm WAD CN, solutions were prepared with concentrations 10, 50 and 100 ppm WAD CN.

4.2.1 Volume of ligand exchange reagent

The volume of LEX reagent to add to approximately100 mL filtrate in the Cynoprobe cell was calculated based on the anticipated maximum WAD cyanide concentration of laboratory test standards and plant trial filtrates.

Table 4.1 below shows the expected metal concentration for 1000 ppm CN standard solutions. Copper, nickel and zinc solutions were considered since these are the WAD metals most prevalent in actual gold leach and discharge solutions. Based on 100% excess (metal-ligand molar ratio of 1:2), 4 mL 20% LEX reagent should be dosed to 100 mL solution in Cynoprobe cell to recover 1000 ppm WAD cyanide.

Table 4.1 Volume of LEX reagent required for recovery of 1000 ppm WAD CN from copper, nickel and zinc

Standard solution	Actual metal conc (mg/L)	Actual metal molarity (mmol/L)	LEX reagent conc-1:1 molar ratio (mg/L)	LEX reagent conc-1:2 molar ratio (mg/L)	Volume neat LEX reagent per 100 mL solution (100% excess)	Volume 20% LEX reagent per 100 mL solution (mL)
Cu-CN	528	8.3	1574	3142	0.6	3.1
Ni-CN	564	9.6	1819	3635	0.7	3.6
Zn-CN	654	10.0	1893	3786	0.7	3.7

Table 4.2 below shows the base metal concentrations expected in gold leach solutions. Normal, high and very high base metal concentrations of <80, 300 and >600 mg/L were considered. Based on 100% excess (metal-ligand molar ratio of 1:2), 0.5, 2 and 4 mL 20% LEX reagent, respectively, should be dosed to 100 mL plant filtrate in the Cynoprobe cell.

Table 4.2 Volume of LEX reagent required for recovery of WAD cyanide from gold leach solutions

Base metals in plant leach filtrate	Total metal conc (mg/L)	Total metal molarity (mmol/L)	LEX reagent conc-1:1 molar ratio (mg/L)	LEX reagent conc-1:2 molar ratio (mg/L)	Vol neat LEX reagent per 100 mL plant filtrate (100% excess)	Vol 20% LEX reagent per 100 mL plant filtrate (mL)
Normal base metals	<80	<1.4	250	500	0.1	0.5
High base metals	300	~5	1000	2000	0.4	2
Very high base metals	>600	>10	>2000	>4000	0.8	4

It was anticipated that commercially the Cynoprobe would be required to measure the WAD cyanide concentration of leach filtrates as well as discharge or environmental water solutions. Since excess ligand exchange reagent addition is preferable, considering the metal-cyanide and metal-ligand

stability constant comparison discussed in Section 4.1.3, the volume of 20% LEX reagent to dose to the Cynoprobe cell was standardised to 2 and 4 mL for normal and high base metal concentrations, respectively.

4.2.2 Effect of ligand exchange reagent on Cynoprobe amperometric response

The effect of the ligand exchange reagent on the amperometric detection of cyanide had to be investigated. This was achieved by testing for interferences from the presence of the reagent in blank and cyanide solutions and plotting voltammograms.

4.2.2.1 Voltammograms for sodium cyanide solutions

Voltammograms were plotted by varying the applied potential and recording the current at a resistance of 40.75 Ω (30-3000 ppm CN), using a cylindrical silver electrode with a surface area of approximately 17 cm^2. Figure 4.1, Figure 4.2 and Figure 4.3 show the curves produced for sodium cyanide standards prepared in the laboratory with concentrations of 0.001 M (26 ppm), 0.010 M (260 ppm), and 0.100 M (2600 ppm), at pH 12 and 9.31. The objective was to observe at what applied potentials cyanide may be measured and whether $HCN_{(aq)}$ is also measured by amperometry.

Figure 4.1 **Cynoprobe voltammograms for 0.001 M (26 ppm CN) NaCN solutions at pH 12 and pH 9.31 (40.75 Ω, 35°C, cylindrical silver electrode)**

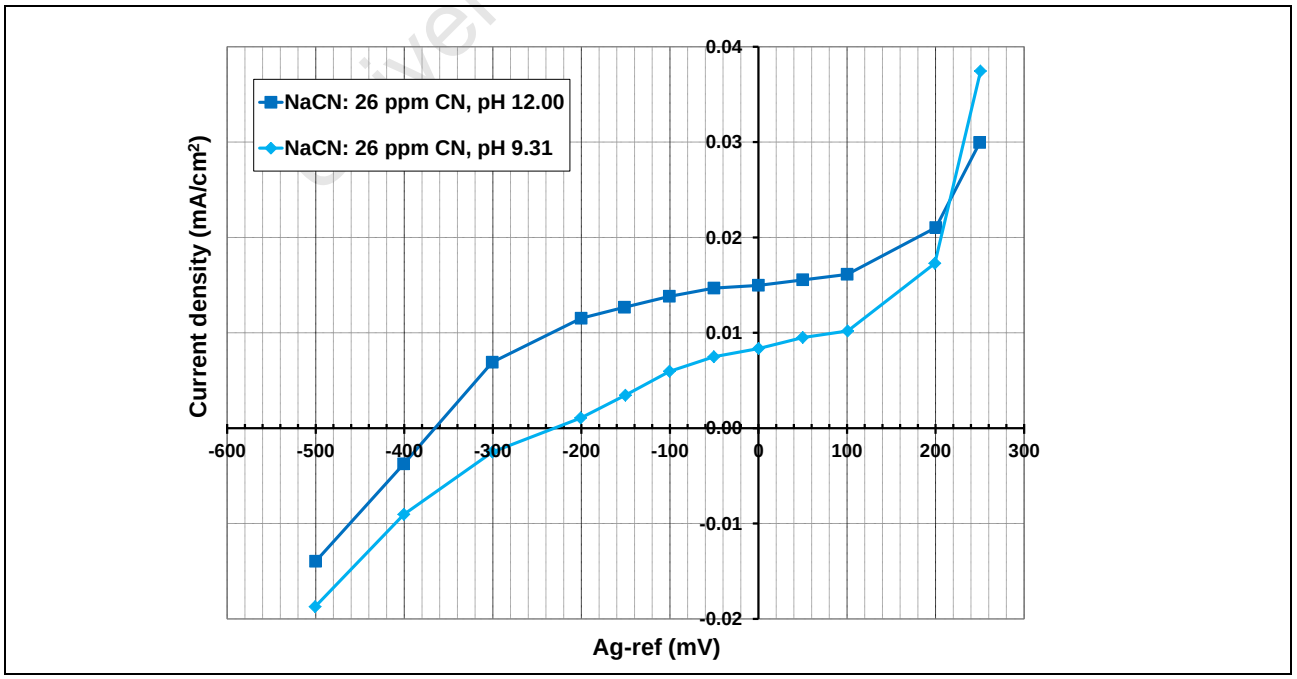


Figure 4.2 **Cynoprobe voltammograms for 0.01 M (260 ppm CN) NaCN solutions at pH 12 and pH 9.31 (40.75 Ω, 35°C, cylindrical silver electrode)**

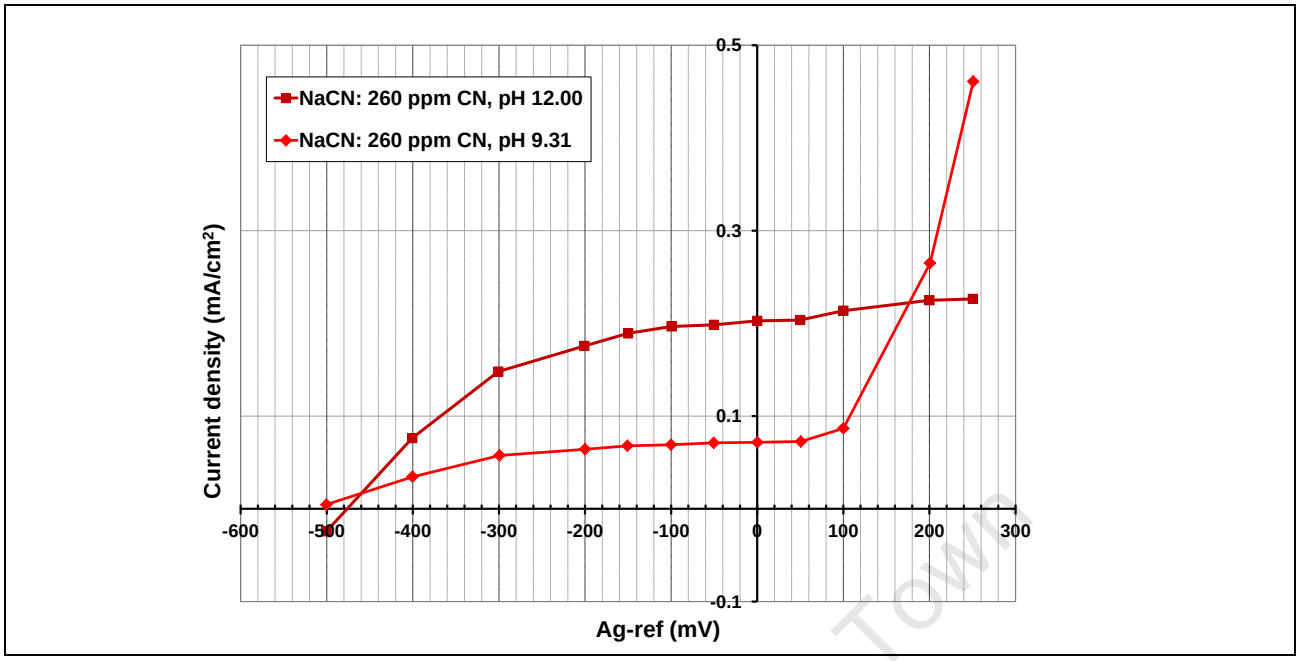
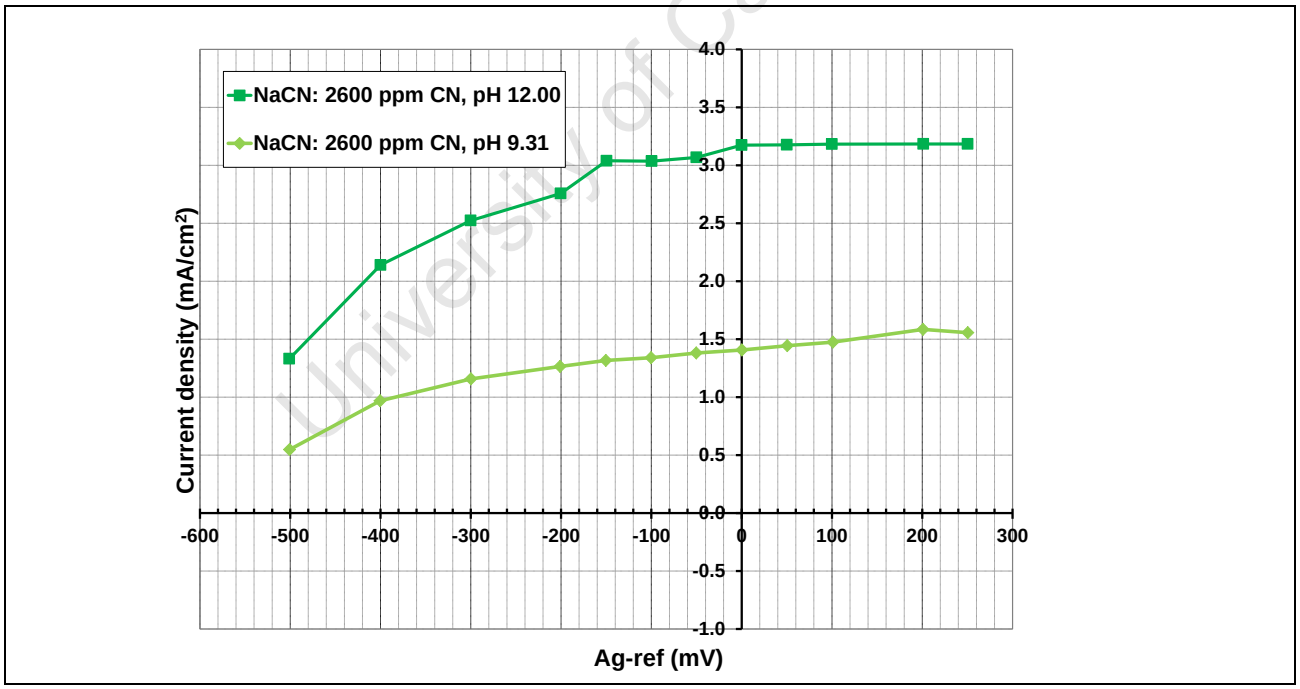


Figure 4.3 **Cynoprobe voltammograms for 0.1 M (2600 ppm CN) NaCN solutions at pH 12 and 9.31 (40.75 Ω, 35°C, cylindrical silver electrode)**



The three figures above demonstrate the Cynoprobe's amperometric response for a wide concentration range, 2.6-2600 ppm CN. All cyanide voltammograms are characteristically flat between -150 mV and 100 mV due to the limiting current from the oxidation of silver by cyanide. Below -200 mV, significant reduction of oxygen occurs on the silver electrode (negative current) and thus the resultant measured current is the current due to silver oxidation by cyanide less the oxygen

reduction current. At high potentials, 100-300 mV, the oxidation of hydroxyl ions to form silver oxides interferes with the cyanide measurement. Therefore, potentials below -250 mV and above 100 mV cannot be used for cyanide measurement, due to the respective interference of oxygen and hydroxyl ions. Historically, the Cynoprobe has been configured to measure free cyanide by applying a voltage of 0 mV.

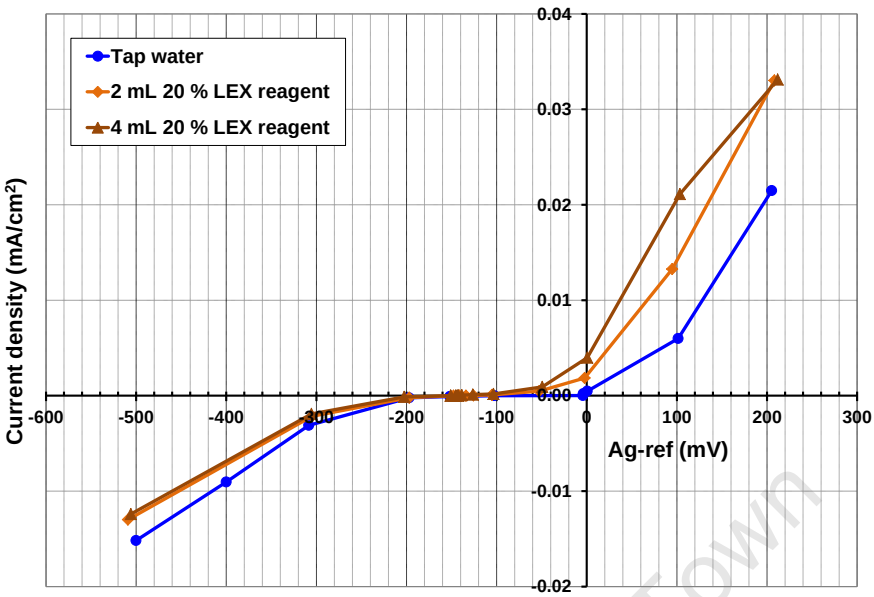
At pH 9.31, cyanide is theoretically present in aqueous solution in equal amounts of CN^- and $HCN_{(aq)}$ (Equation 2.2). The voltammograms for all three concentrations show that at pH 9.31 approximately only half the free cyanide in solution is measured. Therefore, it is clear that $HCN_{(aq)}$ is not oxidised by the working silver electrode and does not contribute to the amperometric response. The Cynoprobe only measures the CN^- ion which is essentially the cyanide available to leach gold. Therefore, no pH adjustment is required to measure the cyanide available to leach gold. However, to recover all free cyanide the pH of the solution should be adjusted to 12 prior to measurement in the amperometric cell.

4.2.2.2 Voltammograms for LEX reagent

4.2.2.2.1 Blank solutions

Voltammograms for the LEX reagent in deionised water were generated at 4020 Ω (0.3-30 ppm), using a cylindrical silver electrode (surface area approximately 17 cm). 2 and 4 mL of 20% LEX reagent were added per 100 mL water in the Cynoprobe amperometric cell.

Figure 4.4 **Cynoprobe voltammograms for LEX reagent in water (4020 Ω, 35ºC, cylindrical silver electrode)**



According to both curves in Figure 4.4, the LEX reagent interferes with the measurement of cyanide at an applied potential of 0 mV. For 2-4 mL 20% LEX reagent this interference was observed to be equivalent to between 2-7 ppm CN. While there is no current for the tap water up to 0 mV, it appears that the LEX reagent begins to react with silver between -200 and -100 mV. Table 4.3 below shows that 0 mA/cm^2 was recorded at approximately -130 and -144 mV for 2 and 4 mL 20% LEX reagent respectively. Therefore, since the cyanide voltammograms (Figure 4.1, Figure 4.2 and Figure 4.3) are still flat at this voltage, WAD cyanide should be measured at approximately -140 mV (configured for each instrument) in order to eliminate any interference from the ligand exchange reagent.

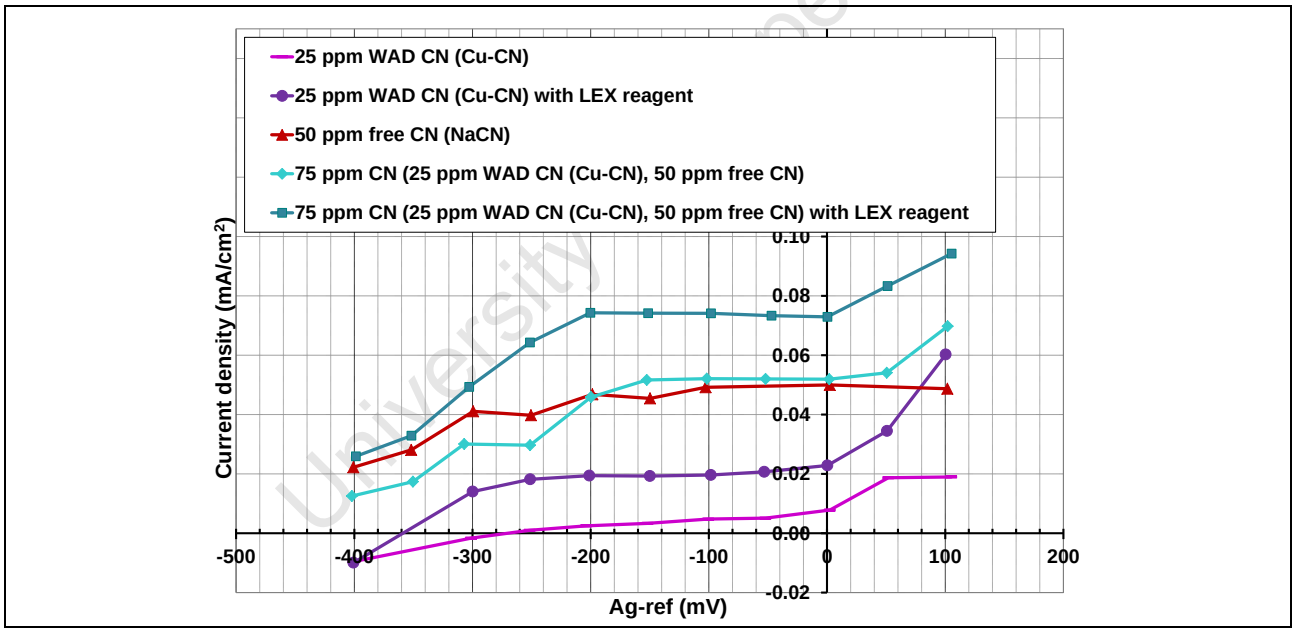
Table 4.3 **Applied potential with resulting current densities for 2 and 4 mL 20% LEX reagent close to the point of no interference (zero current)**

2 mL 20% LEX reagent		4 mL 20% LEX reagent	
Set-point voltage (mV)	**Recorded current density (mA/cm^2)**	**Set-point voltage (mV)**	**Recorded current density (mA/cm^2)**
-141.1	-3.80E-06	-145.51	-3.47E-06
-133.95	-3.66E-06	-144.95	-3.09E-06
-125.68	2.93E-05	-143.01	9.34E-06
-105.08	8.64E-05	-142.43	1.58E-05

4.2.2.2.2 Cyanide solutions

Voltammograms for free and copper cyanide solutions, with and without LEX reagent were generated at 354.2 Ω (3-300 ppm), using a cylindrical silver electrode (surface area approximately 17 cm^2), shown in Figure 4.5. The liberation of cyanide from 25 ppm WAD CN copper cyanide solution by LEX reagent is clearly shown by the curves for the solutions without and with the addition of 2 mL of 20% LEX reagent. Using the 50 ppm free cyanide curve as a reference point and assuming direct proportionality between concentration and current density (acceptable assumption over a small concentration range) ~91% WAD cyanide was liberated by the LEX reagent. Similarly, the 75 ppm WAD cyanide solution consisting of 50 ppm free cyanide and 25 ppm cyanide associated with copper, showed ~97% liberation. Excellent overall recoveries were therefore obtained from both solutions.

Figure 4.5 **Cynoprobe voltammograms for free and copper cyanide solutions without and with 2 mL 20% LEX reagent addition at pH 12 (354.2 Ω, 35ºC, cylindrical silver electrode)**

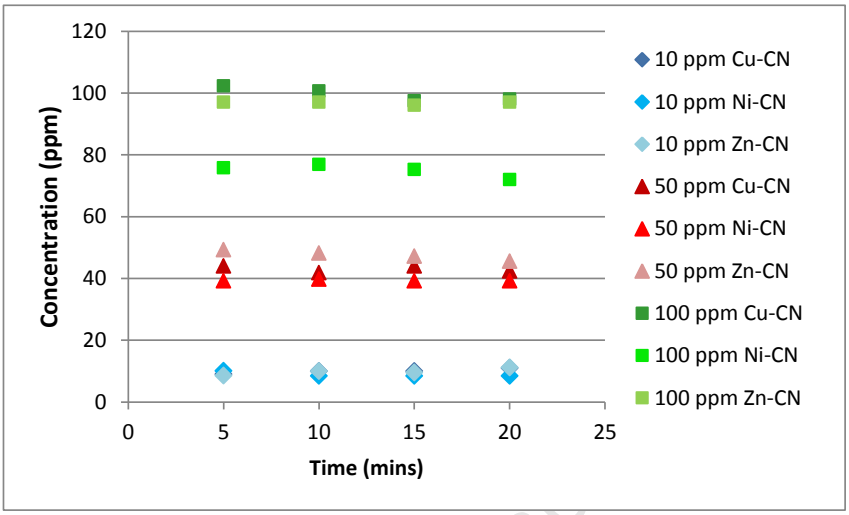


4.2.3 Ligand exchange reagent metal cyanide solution contact times

To determine if the LEX reagent - metal cyanide contact time has any effect on the liberation of cyanide, 10, 50 and 100 ppm pure metal WAD cyanide solutions prepared from copper, nickel and zinc cyanide salts were analysed in the Cynoprobe after 2 mL 20% LEX reagent addition. The solutions were analysed using Cynoprobe v1.0 with potentiostat board v1.0 (1000 Ω resistance, 5-100 ppm CN, 35ºC) and the glass amperometric cell with cylindrical electrode. Cynoprobe readings were taken at five minute intervals for 20 minutes. The recoveries shown in Figure 4.6 do not

increase with time, if anything they decrease slightly. The ligand exchange reaction appeared to take place within a few minutes so long contact times should not be necessary. The software was therefore configured to include an agitation time after LEX reagent addition in order to ensure sufficient mixing and an overall reaction time of approximately 5 minutes before measurement.

Figure 4.6 The effect of contact time on cyanide recovery

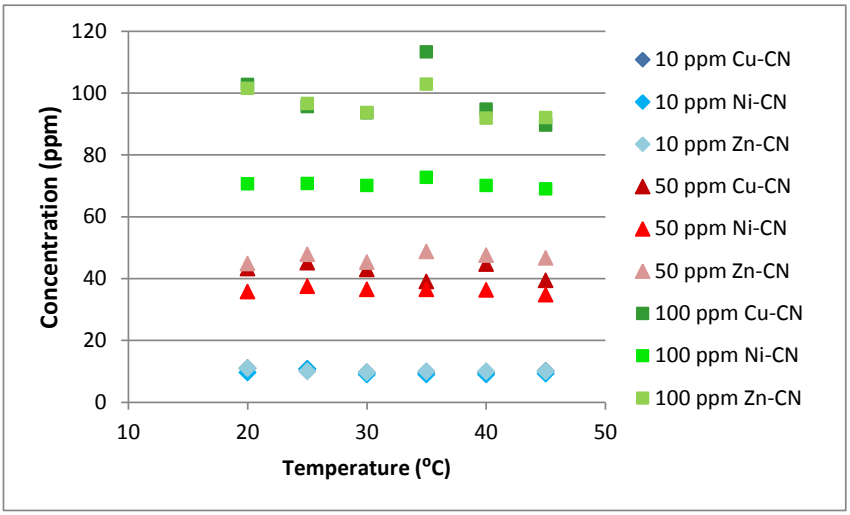


4.2.4 Temperature

Liberation of cyanide from 10, 50 and 100 ppm WAD CN, copper, nickel and zinc cyanide standards was investigated for temperatures ranging from 20-45 °C. The minimum temperature was selected considering that in very cold locations such as in Russia gold plants are often enclosed and solutions below 20°C may be heated in the instrument before measurement. The solutions were analysed using Cynoprobe v1.0 with potentiostat board v1.0 (1000 Ω resistance, 10-100 ppm CN) and the glass amperometric cell with cylindrical electrode.

Figure 4.7 below shows the recoveries obtained from the addition of 2 mL 20% LEX reagent per 100 mL solution. Temperature did not appear to have a dramatic effect on driving or inhibiting the ligand exchange reaction. However, the results for 50 and 100 ppm showed a possible optimal temperature of 35 °C. Though greater recoveries were obtained at 35 °C, it also appeared that the system was most sensitive to small fluctuations in temperature around 35 °C, which became more pronounced as the concentration increased. Temperature was excluded as a variable by controlling the filtrate temperature to a chosen fixed value; 35 °C for laboratory experiments.

Figure 4.7 The effect of temperature on cyanide recovery



4.2.5 Optimised parameters

The technique was found to be robust because of its insensitivity to contact time (5-20 minutes) and temperature (20-35ºC). Adjustment of set-point temperature according to location temperature and season should not adversely affect WAD cyanide recovery.

For laboratory experiments, the parameters discussed above were optimised as follows:

- Volume LEX reagent - 2 mL 20% LEX reagent per 100 mL solution in the Cynoprobe cell.
- Potentiostat board applied potential - approximately -140 mV.
- LEX reagent reaction time - approximately 5 minutes.
- Set-point temperature - 35ºC.

4.3 THE CYNOPROBE'S INITIAL PRECISION AND RECOVERY OF WAD CYANIDE

The instrument's initial precision and recovery for WAD cyanide determination was determined from pure and combination metal cyanide standards. Pure copper, nickel, zinc and silver cyanide solutions, as well as a synthetic representative of gold plant solution consisting of 40% free cyanide, 40% copper cyanide and 20% nickel cyanide were analysed. For completeness, cyanide recoveries from the SAD cyanides, ferrocyanide and ferricyanide were also tested. The mean, standard deviation and percent recoveries were calculated from the analysis of seven replicates (ASTM D-6888-04 recommends the analysis of four replicates; OIA-1677 recommends the analysis of seven replicates). Instrument precision and repeatability was determined by calculating the relative standard deviation from the analysis of solutions four times between four instruments.

4.3.1 WAD cyanide recovery from pure metal solutions

4.3.1.1 Percent recoveries from pure metal solutions

The effectiveness of the LEX reagent at liberating WAD cyanide from copper, nickel, zinc and silver was tested for pure metal solutions with both high and low WAD cyanide concentrations, that incorporate ICMI regulatory concentration limits, namely 0.5, 10, 25, 50 and 100 ppm WAD CN, at pH 12.00. Copper, nickel and zinc cyanide solutions were analysed in Cynoprobe v2.0, using the potentiostat board v1.0. Two separate calibrations at different resistances were performed for the analysis of low (0.5 ppm) and high concentration (10, 25, 50 and 100 ppm) standards, namely 10 000 Ω (0.3-10 ppm CN) and 1000 Ω (5-100 ppm CN) respectively. Silver cyanide recoveries were determined later using the new potentiostat board; 4020 Ω resistor (0.4-30 ppm) and 1214 Ω resistor (10-100 ppm).

Table 4.4 shows the Cynoprobe's free and WAD cyanide determination of each pure metal cyanide solution. The average Cynoprobe reading obtained by analysing each solution at least seven times, before and after LEX reagent addition (2 mL 20% LEX reagent per 100 mL solution), at 35 °C is displayed. The Cynoprobe's free cyanide reading may be compared to the theoretical free cyanide concentrations predicted by a thermodynamic speciation model, using stability constants. Table 4.5 shows the theoretical free cyanide expected to be present in each solution, according to the Mintek speciation spread-sheet (see Table B.1, Table B.2, Table B.3 and Table B.4 in Appendix B for full cyanide speciation).

Table 4.4 Species-dependent cyanide determination in the Cynoprobe before and after ligand exchange reagent addition

Species	Cyanide concentration (ppm)									
	0.5 ppm		10 ppm		25 ppm		50 ppm		100 ppm	
$[Cu(CN)_4]^{2-}$	0.26	0.46	5.29	9.57	13.43	22.43	20.85	45.84	35.60	95.30
$[Ni(CN)_4]^{2-}$	0.24	0.41	0.00	9.07	3.48	19.06	13.25	39.75	10.36	72.84
$[Zn(CN)_4]^{2-}$	0.30	0.44	4.21	9.71	12.27	22.26	28.78	47.04	54.89	95.83
$[Ag(CN)_4]^{2-}$	0.28	0.46	8.42	9.84	21.25	24.36	44.99	49.84	90.06	97.14

Table 4.5 Theoretical free cyanide speciation of pure metal cyanide solutions according to the Mintek speciation spread-sheet (pH 12, 25ºC)

WAD cyanide concentration (ppm)	Theoretical species-dependent free cyanide concentrations (ppm)			
	Cu-CN	Ni-CN	Zn-CN	Ag-CN
0.5	0.19	0.01	0.50	0.00
10	2.68	0.05	9.67	0.01
25	6.45	0.09	18.97	0.02
50	12.65	0.13	26.05	0.04
100	24.97	0.20	33.23	0.08

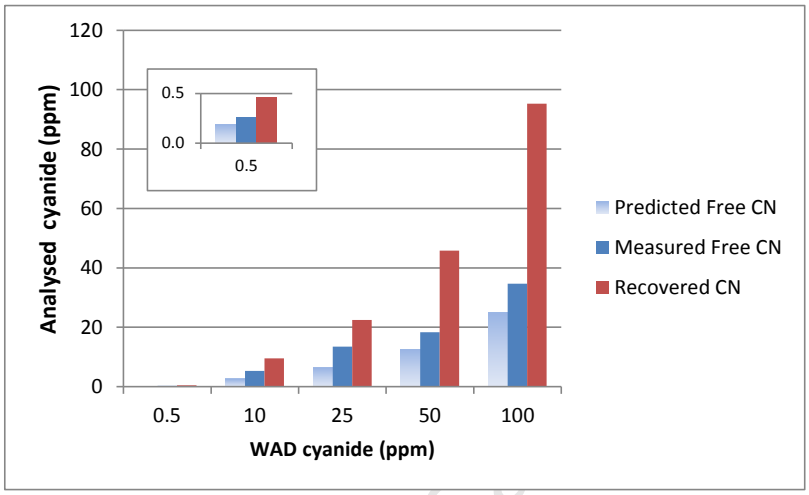
For easier interpretation, a graphical representation of the data in Table 4.4 and Table 4.5 above is shown below in Figure 4.8, Figure 4.9, Figure 4.10 and Figure 4.11. The WAD cyanide readings show the LEX reagent's effectiveness at liberating cyanide from pure metal solutions at 35 °C. Though 100% recovery is not obtained there is clearly a difference between the readings before and after LEX reagent addition. The exact percent recoveries are shown in 0 and discussed below.

There is clearly not much correlation between the theoretical values and the measured concentrations measured in the Cynoprobe, before LEX reagent addition. For all solutions except low concentrations of zinc cyanide (0.5, 10 and 25 ppm), the free cyanide measured by the Cynoprobe in solutions was higher than the predicted value. This may be explained by two hypotheses. First hypothesis; the actual free cyanide present in real solutions is greater than the theoretical value. Stability constants vary between literature sources and are determined under standard conditions. The analysis temperature of real solutions (35ºC) was greater than the temperature at which constants were determined (25ºC). The actual ionic strength was not considered. Theoretical thermodynamics are at best semi-quantitative if effects of the ionic strength and temperature are not considered. Second hypothesis; some cyanide that is loosely bound in the metal cyanide complexes is likely to react with silver and contribute to the amperometric response. This is proved by van der Merwe and Breuer (2011), where the Cynoprobe's free cyanide analysis of copper and zinc cyanide solutions is examined in detail.

For all copper cyanide solutions, except 0.5 ppm where the cyanide becomes evenly distributed between all species, the predominant species in solution was predicted to be $[Cu(CN)_3]^{2-}$ (>70%), followed by CN^- (~25%) and small portions of $[Cu(CN)_4]^{3-}$ (~2%) and $[Cu(CN)_2]^-$ (<1%) (Table B.1, Appendix B). The fourth and third cyanide are most easily liberated from copper, explained by the difference in stability constants from Table 2.1, $\log \beta_4 - \log \beta_3 = 1.7$ and $\log \beta_3 - \log \beta_2 = 4.6$ (Lurje, 1971), and probably account for the cyanide recovered by the LEX reagent from copper. The free cyanide readings obtained for the copper cyanide solution are all greater than those predicted by

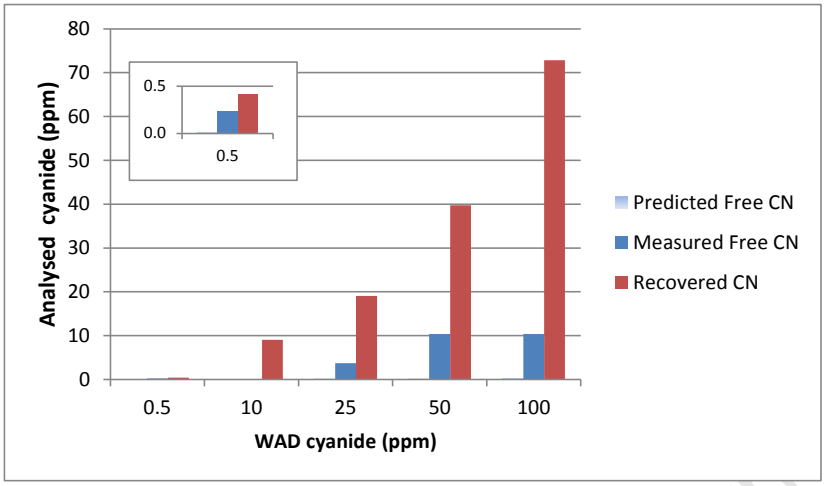
the theoretical model. It is possible that in the presence of copper the Cynoprobe recovers more than just the free cyanide. Some cyanide bound to copper, for example the fourth cyanide bound in the tetracyanide species, is also likely to react with the silver electrode (van der Merwe and Breuer, 2011).

Figure 4.8 **A comparison of the theoretical and measured free cyanide with the recovered cyanide by the LEX reagent, as analysed in the Cynoprobe at 35ºC, for copper cyanide solutions**



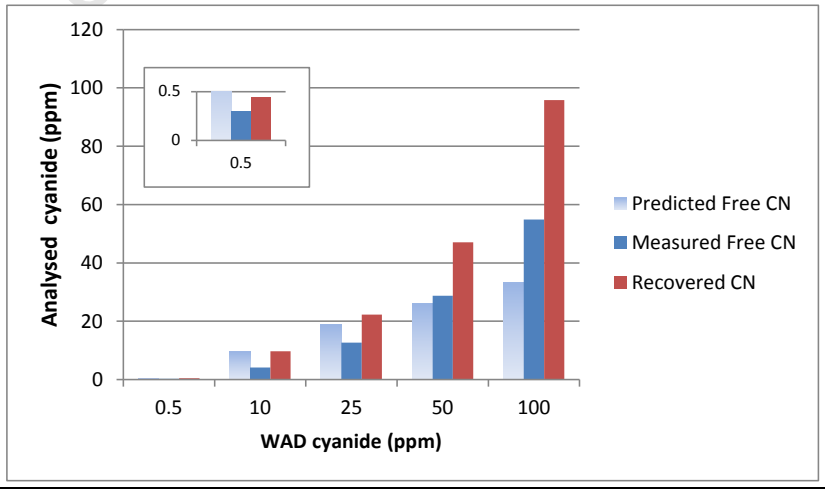
The least free cyanide was present in the nickel cyanide solutions. Hence the cyanide recovered by the LEX reagent appears most pronounced in these solutions. Unlike copper, cyanide tends to form only one species with nickel, the tetracyanate species, $[Ni(CN)_4]^{2-}$. This can be seen by the predicted speciation for all nickel cyanide solutions (Table B.2, Appendix B). For all concentrations the predominant species in solution was predicted to be $[Ni(CN)_4]^{2-}$ (92-99%), with small portions of $[Ni(CN)_3]^{-}$ (0.3-6%) and CN^{-} (0.2-2%). As the total cyanide concentration decreases so the percent metal cyanide seems to increase (Table B.2, Appendix B).

Figure 4.9 **A comparison of the theoretical and measured free cyanide with the recovered cyanide by the LEX reagent, as analysed in the Cynoprobe at 35ºC, for nickel cyanide solutions**



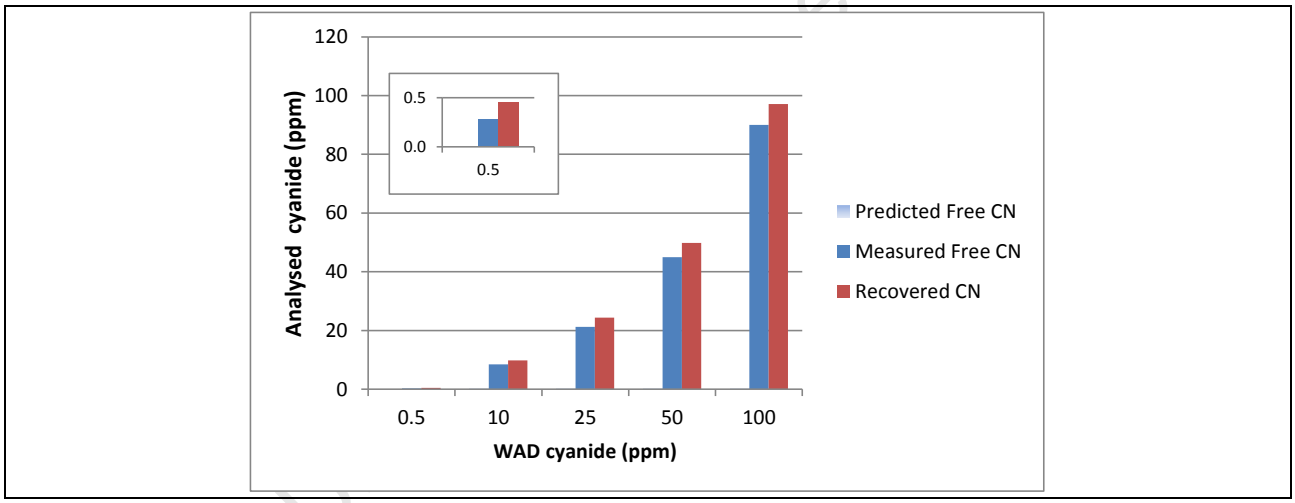
Zinc dissolves in alkaline cyanide solutions to form $[Zn(CN)_4]^{2-}$ predominantly, small percentages of $[Zn(CN)_3]^{-}$ and various zinc hydroxide species depending on the pH (hydroxide species increase with increasing pH). According to the theoretical speciation (Table B.3, Appendix B), $[Zn(CN)_4]^{2-}$ is the predominant species in solution for 100 ppm WAD CN, however with decreasing concentration it drops and free cyanide becomes the predominant species. Theoretically, the hydroxide species account for 10% at 100 ppm WAD CN, but also decrease with decreasing concentration, to 0% for 0.5 ppm WAD CN. The actual free cyanide concentrations measured by the Cynoprobe do not follow this trend and consistently account for approximately 50% of the total cyanide for all concentrations. This phenomenon is further examined by van der Merwe and Breuer (2011).

Figure 4.10 **A comparison of the theoretical and measured free cyanide with the recovered cyanide by the LEX reagent, as analysed in the Cynoprobe at 35ºC, for zinc cyanide solutions**



Since the silver cyanide salt is not commercially available and could not be purchased, the solutions were prepared by mixing AgCN and NaCN (1:1 cyanide molar ratio) with the intent of forming aqueous $[Ag(CN)_2]^-$. According to the theoretical speciation show in Table B.4 (Appendix B), $[Ag(CN)_2]^-$ should account for 99% of the total cyanide in all solutions. However, as shown in Figure 4.11, the Cynoprobe's free cyanide measurements were high (>80% for all solutions except 0.5 ppm). This suggests that aqueous $[Ag(CN)_2]^-$ was not formed in solution as intended, possibly due to hydrolysis with Ag_2O formation and CN^- liberation. The portion of bound cyanide was hence low, leaving little cyanide to be liberated by the LEX reagent. Though very high recoveries were obtained for silver cyanide, they should not lead to the interpretation that the LEX reagent is most specific for silver. Silver tenor in gold cyanide solutions is generally low and hence is less important in this study. Application to high silver cases would require site-specific method development, with actual plant filtrate if possible.

Figure 4.11 **A comparison of the theoretical and measured free cyanide with the recovered cyanide by the LEX reagent, as analysed in the Cynoprobe at 35ºC, for silver cyanide solutions**



0 and Figure 4.12 below show the overall percent WAD cyanide recoveries obtained for each metal cyanide solution analysed in the Cynoprobe after 2 mL 20% LEX reagent addition per 100 mL solution. 0 and Figure 4.12 show the percent recoveries of bound cyanide based on Cynoprobe free cyanide readings.

According to ASTM D-6888-04, for a reference material containing 70 ppb available cyanide the mean should range from 48.8-79.6 ppb (70-114%). These limits are recommended for an initial demonstration of laboratory capability and are applicable for 2-400 ppb. They give one an idea of recoveries achieved by other laboratories for low concentrations. The Cynoprobe's overall cyanide recoveries from cyanide solutions (with concentrations approximately 250 times the maximum limit

of the laboratory method) presented in 0 fall within the limits specified by ASTM D-6888-04; 90-96%, 73-91%, 90-97% and 91-100% for copper, nickel, zinc and silver, respectively. On average, overall recoveries were approximately 93, 80, 93 and 97% for copper, nickel, zinc and silver, respectively. Relative standard deviations <8.6% were obtained, which were well within the laboratory method specification of <11.1%.

Although the overall percent recoveries shown in Figure 4.12 indicate that cyanide is most readily liberated from silver followed by copper, zinc and finally nickel, the recoveries of bound cyanide shown in Figure 4.12 indicate that cyanide is most readily liberated from copper, followed by zinc, silver and finally nickel. On average, recoveries from copper, zinc and silver were approximately 86, 85 and 84%, respectively, and those from nickel were approximately 75%. The high recoveries for copper were expected because of the LEX reagent's selectivity for copper discussed in Section 4.1.3. Good recoveries from zinc were expected as cyanide is weakly bound to zinc; $\log \beta_4 - \log \beta_3 = 3.57$, $\log \beta_3 - \log \beta_2 = 4.98$ and $\log \beta_2 = 11.07$ (see Table 2.1) and the stability of the LEX reagent complex is comparable (Smith and Martell, 1975). Recoveries from silver were surprisingly high, but should be interpreted considering the low concentrations of $[Ag(CN)_2]^-$ in solution due to slow kinetics of formation. Low recoveries from nickel can be explained by the existence of the sole nickel tetracyanide species which is highly stable ($\log \beta_4 = 30.22$) over the nickel LEX reagent complex (Smith and Martell, 1975).

For all metals, recoveries of over 90% were obtained from 10 ppm. This is most likely due to the activity or 'chemical effectiveness' of the system. The activity of a cyanide ion, rather than the concentration, determines the rate and extent of chemical reactions. The activity coefficient depends on the ionic strength of the solution. At lower concentrations favourable collisions between reactants are more frequent. However, at higher concentrations increased total ionic strength tends to inhibit favourable collisions.

For copper, zinc and silver high overall recoveries (>88%) were obtained for 0.5 ppm. However, the percent recoveries based on the cyanide bound were significantly lower. At low concentrations experimental and instrument error is amplified. The Cynoprobe's accuracy at such low concentrations has since been improved by redesigning the potentiostat board, the details of which are beyond the scope of this thesis.

Table 4.6 **Overall recoveries and relative standard deviations for pure metal cyanide solutions (35ºC)**

Species	Overall percent recoveries and relative standard deviations				
	0.5 ppm	10 ppm	25 ppm	50 ppm	100 ppm
$[Cu(CN)_4]^{2-}$	91.6% (3.3%)	95.7% (8.2%)	89.7% (8.5%)	91.7% (5.5%)	95.3% (3.0%)
$[Ni(CN)_4]^{2-}$	82.8% (2.3%)	90.7% (7.7%)	76.2% (6.5%)	79.5% (2.4%)	72.8% (4.4%)
$[Zn(CN)_4]^{2-}$	88.9% (2.6%)	97.1% (5.0%)	89.1% (5.9%)	94.1% (3.3%)	95.8% (2.0%)
$[Ag(CN)_4]^{2-}$	91.1% (2.4%)	98.4% (0.6%)	97.4% (1.0%)	99.7% (0.7%)	97.1% (0.7%)

Values are percent recoveries; values in parentheses are percent relative standard deviations.

Figure 4.12 **Species-dependent overall cyanide recoveries**

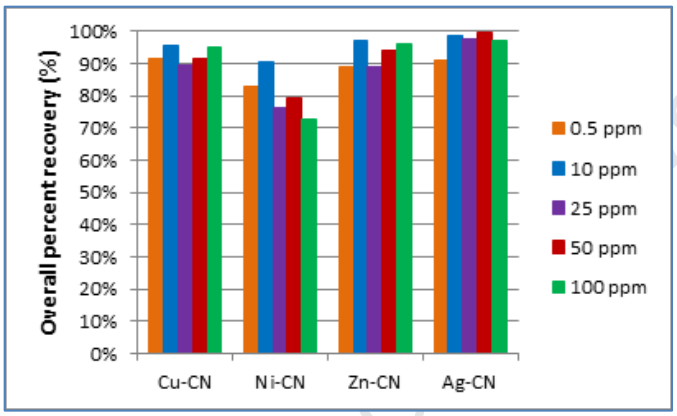
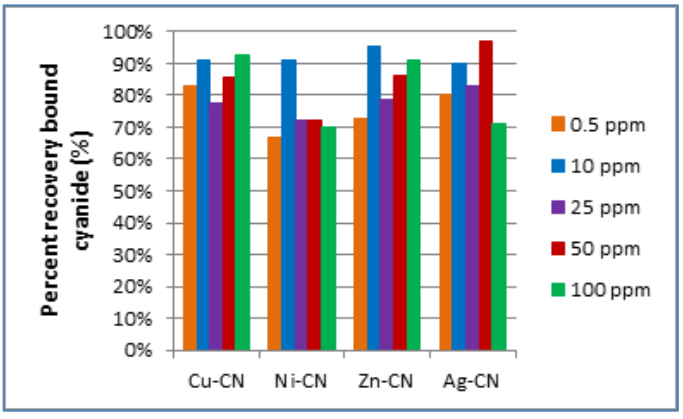


Table 4.7 **Recoveries based on bound cyanide as analysed in the Cynoprobe for pure metal cyanide solutions (35ºC)**

Species	Percent recoveries bound cyanide				
	0.5 ppm	10 ppm	25 ppm	50 ppm	100 ppm
$[Cu(CN)_4]^{2-}$	82.8%	90.9%	77.8%	85.7%	92.7%
$[Ni(CN)_4]^{2-}$	67.0%	90.7%	72.4%	72.1%	69.7%
$[Zn(CN)_4]^{2-}$	72.5%	95.1%	78.5%	86.0%	90.8%
$[Ag(CN)_4]^{2-}$	80.1%	89.9%	82.9%	96.9%	71.2%

Figure 4.13 **Species-dependent bound cyanide recoveries based on the Cynoprobe's free cyanide reading**



For completeness, cyanide recoveries from the SAD cyanides, ferro and ferri-cyanide were tested. The Cynoprobe reading before and after the addition of ligand exchange reagent to Fe^{2+} and Fe^{3+} cyanide solutions with concentrations 0.5, 10, 25, 50 and 100 ppm total CN was 0 ppm. As expected, no cyanide is released from iron in the presence of the ligand exchange reagent. These results were confirmed by CN-ISE.

4.3.1.2 Repeatability of percent recovery and precision

Method OIA-1677 suggests that the average percent recovery (x) and the standard deviation of the percent recovery (s) be calculated from four analysed samples. The quality control acceptance criteria presented in the method are specific for low concentration analysis (0.002-5 ppm). However, they give an idea of the accuracy and precision obtainable for the laboratory method, using proprietary reagents. The recommended on-going recovery range is 82-132% and the initial precision is <5.1% RSD. It should be noted that an online instrument will not be expected to perform to the acceptance criteria of a laboratory method.

Repeatability experiments were performed for 50 ppm pure metal cyanide solutions. Four separate solutions were analysed on different instruments at different times, each calibrated with potentiostat board v1.0 at a resistance of 1000 Ω (5-100 ppm CN). Table 4.8 and Table 4.9 below show the average, overall percent recoveries, standard deviation and relative standard deviations obtained from four readings. Recoveries from zinc, copper and silver ranged from 81-100%. But for 1% this is within the recommended on-going recovery range for the low concentration, laboratory method. Recoveries from nickel are consistently low, on average 75%. For all experiments, the percent relative standard deviation was <4.4%, within Method OIA-1677's recommended precision limit of <5.1%. The relative standard deviation between instruments ranged from 2.1-3.1%.

Table 4.8 Repeatability of overall recoveries obtained for 50 ppm for pure metal cyanide solutions (35ºC)

Species	Percent recoveries				
	Test 1	Test 2	Test 3	Test 4	Average
$[Cu(CN)_4]^{2-}$	81.0%	82.2%	84.8%	95.5%	85.3%
$[Ni(CN)_4]^{2-}$	78.7%	80.8%	79.1%	64.0%	75.2%
$[Zn(CN)_4]^{2-}$	95.1%	100.2%	94.0%	82.5%	93.0%
$[Ag(CN)_4]^{2-}$	99.7%	98.6%	-	-	99.2%

Table 4.9 **Repeatability of standard deviations and relative standard deviations obtained for 50 ppm pure metal cyanide solutions (35ºC)**

Species	Standard deviation and relative standard deviation				
	Test 1	Test 2	Test 3	Test 4	Instrument
$[Cu(CN)_4]^{2-}$	1.02 (2.5%)	0.92 (2.2%)	1.13 (2.7%)	0.50 (1.0%)	1.44 (3.1%)
$[Ni(CN)_4]^{2-}$	0.27 (0.7%)	1.18 (2.9%)	0.84 (2.1%)	1.41 (4.4%)	0.89 (2.1%)
$[Zn(CN)_4]^{2-}$	1.58 (3.3%)	1.40 (2.8%)	1.83 (3.9%)	0.96 (2.3%)	0.92 (2.5%)
$[Ag(CN)_4]^{2-}$	0.45 (1.0%)	1.95 (3.8%)	-	-	1.20 (2.4%)

Values are standard deviations; values in parentheses are percent relative standard deviations.

4.3.1.3 Increasing nickel cyanide recovery

For the concentration range, 0.5-100 ppm, the on-going overall WAD cyanide recoveries from copper, zinc and silver ranged from 81-100%. However, cyanide liberation from nickel was lower, ranging from 64-91%. The effect of excess LEX reagent addition on the liberation of cyanide from nickel was therefore investigated with the intent of increasing recoveries. According to Le Chatelier's principle a change in volume shifts the equilibrium to counteract the imposed change, in so doing promoting the ligand exchange reaction. The Cynoprobe was calibrated with potentiostat board v1.0 at 1000 Ω resistance (5-100 ppm) for each LEX reagent volume. Figure 4.14 below shows the average concentrations obtained after excess LEX reagent addition for nickel cyanide solutions with concentrations of 10, 50 and 100 ppm WAD CN. All three concentration trends increased with reagent volume.

Figure 4.14 **The effect of excess LEX reagent addition on cyanide recovery for from nickel (pH 12, 35ºC)**

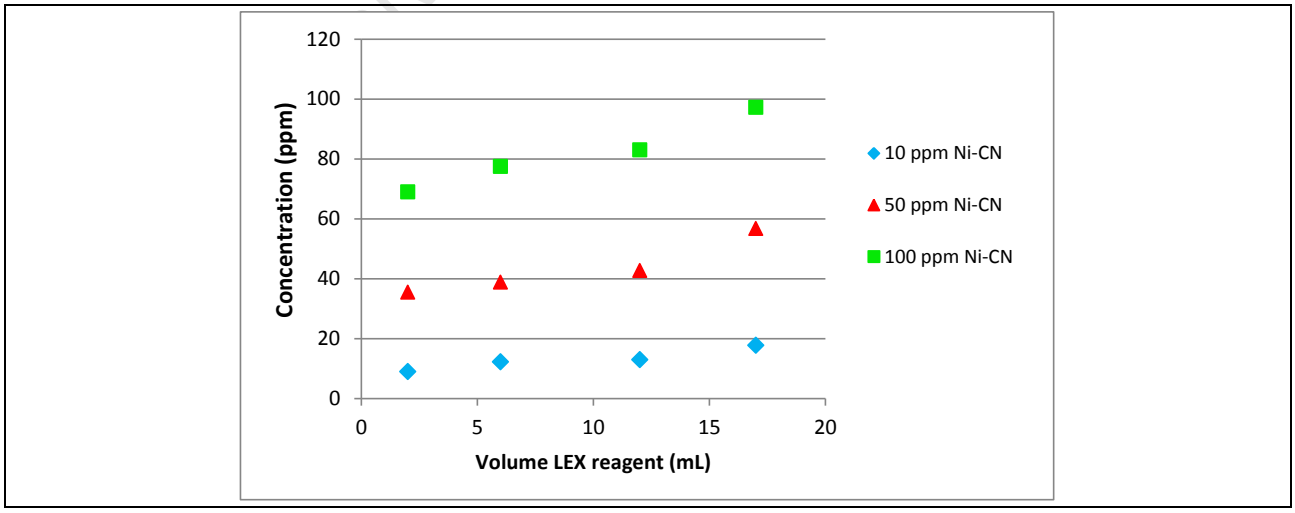


Table 4.10 shows the average overall percent recoveries obtained after 2, 6, 12 and 17 mL 20% LEX reagent addition. For 10 ppm, acceptable recoveries were obtained for 2 mL 20% LEX reagent

addition. For 50 ppm, recoveries increased from 71-113.5%, for 2-17 mL reagent. A volume of 14.5 mL reagent would conceivably produce 100% recovery. Recoveries for 100 ppm increased from 69-97.3%. The larger the concentration, the greater the volume of reagent required to shift the chelation reaction equilibrium. Recoveries from nickel may therefore be increased by the addition of less diluted or neat LEX reagent, rather than large volumes of 20% reagent which would be impractical. For nickel concentrations <56 ppm, 6 mL 10% LEX reagent should produce recoveries ranging from 83-130% for 10-100 ppm WAD CN. In the unlikely case of a gold plant with significant nickel concentrations, the reagent addition should be customised according to the expected WAD cyanide concentration. This would include a slight adjustment of the voltage set point to more negative potentials to ensure that no interference results from high LEX reagent concentrations. A similar argument should hold for copper and site specific optimisation for high copper applications should be considered.

Table 4.10 The effect of excess LEX reagent addition on overall percent cyanide recovery from nickel (pH 12, 35ºC)

WAD cyanide concentration	Volume of 20% LEX reagent			
	2 mL	6 mL	12 mL	17 mL
10 ppm	90.0%	-	-	-
50 ppm	71.0%	77.7%	85.5%	113.5%
100 ppm	69.0%	77.5%	83.0%	97.3%

4.3.2 WAD cyanide recovery from combination metal solutions

4.3.2.1 Accuracy and precision data for combination metal cyanide solutions

Though a negative method bias was observed for nickel cyanide overall, recoveries from low concentrations (10 ppm) were high (90%). ASTM D-6888-04 also reports high recoveries of low concentration (2-400 ppb CN) potassium nickel cyanide (fortified with 100 ppb CN) ranging from 89.9-99.6%. Nickel is associated with precious metals only in trace amounts. In real gold leach and residue solutions it is typically found in concentrations less than 10 ppm. Therefore one would expect at least 90% detection of cyanide bound to nickel in typical gold plant filtrates.

Individual copper, nickel and zinc cyanide standards are hardly representative of a typical gold plant filtrate. A better synthetic representative of an actual post gold leach liquor would be a combination standard consisting of approximately 40% free cyanide, 40% copper cyanide and 20% nickel cyanide with a total cyanide concentration ranging from 0.5-100 ppm. Therefore, percent recoveries were determined for a combination metal standard analysed in the Cynoprobe. Cynoprobe v2.0 with

potentiostat board v1.0 (V_{sp} = -140 mV) was calibrated for high and low concentrations at two different resistances for low and high concentrations; 10 000 Ω (0.3-10 ppm CN) and 1000 Ω (10-100 ppm CN), respectively. Table 4.11 below shows the accuracy and precision data obtained from the free and WAD cyanide analysis of 0.5, 10, 50 and 100 ppm WAD cyanide. The values are an average of seven readings. The instrument is less precise for low concentration analysis, <7% RSD for WAD cyanide analysis of 0.5 and 10 ppm WAD CN, and <5% RSD for free cyanide analysis of 0.5 and 10 ppm. For higher concentrations its precision increased with relative standard deviations <3% for both free and WAD cyanide analysis. For lack of another standard for comparison, the Cynoprobe's precision was compared to the initial precision of the analogous standard test method. According to ASTM D-6888-04, which includes a matrix separation step, an initial of precision of <11.1% was achievable in the laboratory for 2-400 ppb. Though the measurable concentration range of the Cynoprobe in this case was greater than that of ASTM D-6888-04, it demonstrated a greater initial precision than the laboratory test method.

Table 4.11 Combination metal cyanide standard cyanide free and WAD cyanide readings

True concentration (ppm)	Theoretical free CN	Mean recovery (ppm)		Standard deviation		Percent RSD	
		Free CN	WAD CN	Free CN	WAD CN	Free CN	WAD CN
0.5	0.27	0.30	0.48	0.01	0.03	4.5%	6.8%
10	5.04	5.83	9.82	0.23	0.64	4.0%	6.5%
50	25.00	25.86	45.94	0.72	0.94	2.8%	2.1%
100	49.85	58.80	97.70	1.39	2.82	2.4%	2.9%

Figure 4.15 below is a graphical representation of the theoretical (Table B.5, Appendix B) and measured free cyanide composition of the combination metal cyanide standard, as well as WAD cyanide liberated by the LEX reagent at 35ºC. As was the case for the pure metal cyanide solutions, the measured free cyanide was greater than the predicted value for all solutions.

Figure 4.15 **A comparison of the theoretical and measured free cyanide with the recovered cyanide by the LEX reagent, as analysed in the Cynoprobe at 35ºC, for combination metal cyanide solutions**

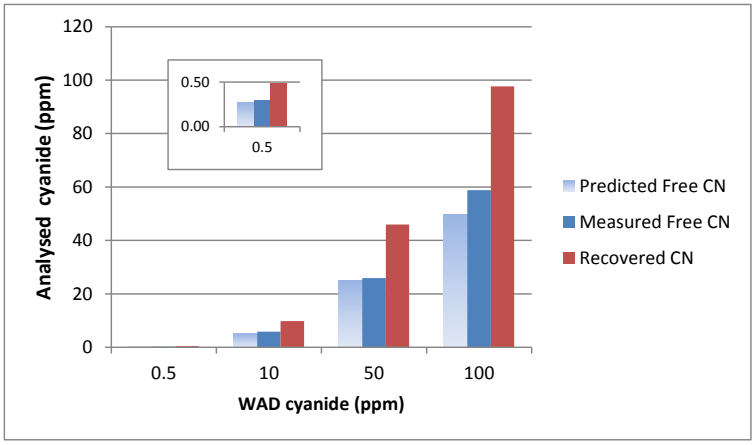
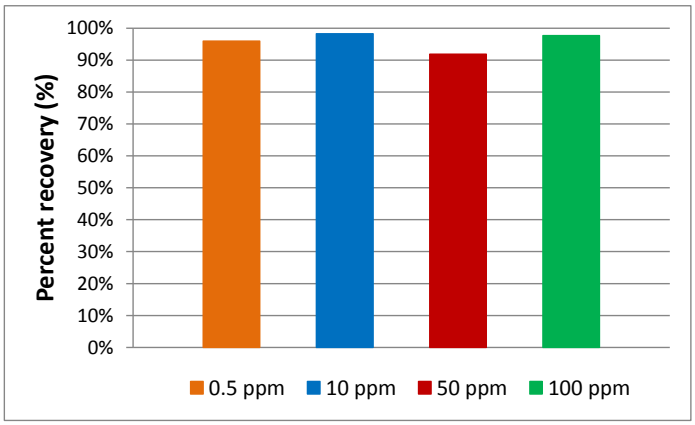


Table 4.12 shows the WAD cyanide recoveries obtained from the analysis of the combination metal cyanide standard. The percent recoveries of bound cyanide based on free cyanide readings from the Cynoprobe were >80% and the overall recoveries were >91% across the entire concentration range (Figure 4.16). Method OIA-1677 recommends an initial recovery range of 92-122%. The Cynoprobe produced an initial accuracy >91% for WAD cyanide analysis of combination metal cyanide solutions with concentrations ranging from 0.5-100 ppm WAD CN.

Table 4.12 **Combination standard cyanide recoveries**

WAD cyanide concentration (ppm)	Percent recovery	
	Overall	Bound cyanide
0.5	95.9%	89.9%
10	98.2%	95.8%
50	91.9%	83.2%
100	97.7%	94.4%

Figure 4.16 **Overall cyanide recoveries from the combination metal cyanide standard**



4.3.2.2 Repeatability of percent recovery and precision

Repeatability experiments were performed for 50 and 100 ppm combination metal cyanide solutions. Four separate solutions were analysed on different instruments at different times. Test 1 and 2 were calibrated with potentiostat board v1.0 at resistances of 1000 Ω and 500 Ω respectively. Test 3 and Test 4 were calibrated with potentiostat board v2.0 at a resistance of 1214 Ω (10-100 ppm CN). 2 mL 20% LEX reagent was added per 100 mL solution. Table 4.13 and Table 4.14 below show the average overall percent recoveries, standard deviation and relative standard deviations obtained from at least 7 readings. Recoveries ranged from ~82-96% and the relative standard deviation was <8%. Recoveries between instruments were variable producing an instrument deviation of <7%. According to Method OIA-1677 an on-going recovery range of 82-132% was achieved for low concentration analysis in a controlled environment. The Cynoprobe therefore produced an on-going accuracy of >82% for WAD cyanide analysis of combination metal cyanide solutions with concentrations 50 and 100 ppm WAD CN.

Table 4.13 Repeatability of accuracy and precision data for 50 ppm combination metal cyanide solutions (35ºC)

	Test 1	Test 2	Test 3	Test 4	Instrument
Percent recovery	85.4%	87.9%	92.5%	85.8%	87.9%
Standard deviation	0.65	1.78	3.68	3.40	1.63
RSD	1.0%	4.0%	8.0%	7.9%	3.7%

Table 4.14 Repeatability of accuracy and precision data for 100 ppm combination metal cyanide solutions (35ºC)

	Test 1	Test 2	Test 3	Test 4	Instrument
Percent recovery	95.9	90.2	95.9	82.8	91.2%
Standard deviation	4.72	4.04	1.20	3.64	6.20
RSD	4.9%	4.5%	1.3%	4.4%	6.8%

4.4 LIMITS OF DETECTION AND QUANTIFICATION FOR DYNAMIC CONCENTRATION RANGES BASED ON RESISTANCE

Any instrument should undergo quality control procedures in order to determine its capability. This includes a determination of its limit of detection (LoD) or detection limit (DL), and limit of quantification (LoQ) or lower quantification limit (LQL), as well as its initial accuracy and precision.

The Cynoprobe may be configured to measure various concentration ranges, depending on the

resistance setting of the potentiostat board. Since 2005, two potentiostat board versions have been utilised in Cynoprobe instruments. Table 4.15 shows the dynamic concentration range for each current sensing resistance, based on the potentiostat board output electronics. It was therefore necessary to determine the detection and quantification limits for each resistance on each potentiostat board.

Table 4.15 Resistances and dynamic measurable concentration ranges for Potentiostat board v1.0 and v2.0

Potentiostat board v1.0		Potentiostat board v2.0	
Resistance (Ω)	**Dynamic concentration range (ppm)**	**Resistance (Ω)**	**Dynamic concentration range (ppm)**
10 000	0-20	4020	0.3–30
1000	0-100	1214	1–100
500	0-300	354.2	3-300
100	0-1000	117.1	10–1000
10	0-2000	40.75	30–3000

Pure sodium cyanide standards were prepared within each of the concentration ranges shown in Table 4.15 and the solutions were analysed at least ten times in the Cynoprobe. A blank solution of tap water at pH 12 was also analysed. The solutions were analysed at an applied voltage of 0 mV and at a temperature set-point of 34ºC with the glass amperometric cell and cylindrical electrode in Cynoprobe v2.0.

Thereafter data was generated to determine the instrument's accuracy and precision in each range. The Cynoprobe's accuracy was determined by calculating the percent error with respect to the average of three potentiometric titration results. Its precision was determined by calculating the relative standard deviation.

Figure C.1 to Figure C.10 in Appendix C show the percent error and relative standard devations for the dynamic concentration range of each resistance for potenitostat board v1.0 and v2.0. All figures clearly illustrate the compromise on precision and especially accuracy close to the upper and lower concentration limits. The measurable concentration ranges for each resistance were then determined by calcualting the upper and lower quantification limits.

An instrument's detection limit is the smallest concentration of analyte that can be detected with statistical confidence. It was calculated according to Equation 3.6 in Section 3.2.6.5 which considers the blank signal and standard deviation. In this case, the factor accounting for the desired

confidence level of 95% for laboratory standards was 1.645, which corresponds to a significance level of alpha = 0.0548. According to the American Chemical Society's Committee on Environmental Analytical Chemistry the quantification limit is defined as the lowest concentration at which the analyte can be quantified. It may be equivalent to or greater than the detection limit. It was calculated according to Equation 3.7 for very high resistances such as 10 000 and 4020 Ω and Equation 3.8 for all other resistances. Table 4.16 below shows the detection limits; lower quantification limits (LQL) and upper quantification limits (UQL), relative standard deviations (RSD) and uncertainty that were calculated for each resistance. For high resistances, the Cynoprobe was calibrated over two concentration ranges in order to obtain lower quantification limits. The upper quantification limits were chosen in accordance with percentage errors of less than 5%. For all resistances the Cynoprobe v2.0's precision was confirmed with a relative standard deviation ≤ 7.2%. An accuracy of 95% can be expected for sodium cyanide solutions. A similar exercise should be repeated for Cynoprobe v3.0 that includes an amperometric cell with symmetrical geometry to reduce the variability in the voltage drop due to the resistance of the solution and hence increase accuracy.

Table 4.16 Resistances, measurable concentration ranges and quantification limits for Potentiostat board v1.0 and v2.0

Potentiostat board version	Resistance (Ω)	Measurable range (ppm)	Detection limit (ppm)	LQL (ppm)	UQL (ppm)	Percent RSD	Percent error
V1.0	10 000	0.30-10	0.10	0.30 (0.32)	10	2.9%	4.4%
	1000	5-100	0.36	5 (5.20)	100	4.1%	4.7%
	500	10-250	2.13	10 (12.13)	350	5.3%	4.2%
	100	100-1000	10.17	100 (99.98)	1000	6.2%	3.6%
	10	250-2500	126.31	250 (263.56)	2500	2.8%	4.9%
V2.0	4020	0.10-10	0.04	0.10 (0.10)	10	7.2%	5.0%
	4020	0.40-30	0.26	0.40 (0.37)	30	2.9%	2.9%
	1214	5-50	4.90	5 (6.66)	50	2.6%	4.6%
	1214	10-125	5.77	10 (12.40)	125	3.9%	4.6%
	354.2	20-300	2.55	20 (20.23)	300	3.1%	4.4%
	117.1	20-1000	17.83	20 (19.84)	1000	2.5%	4.9%
	40.75	130-3800	38.34	130 (129.74)	3800	2.3%	4.0%

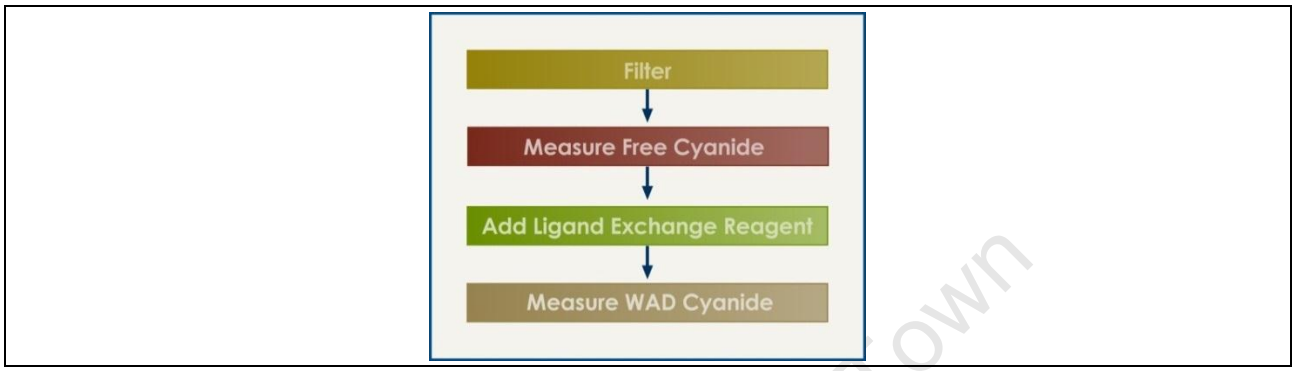
LQL according to Equation 3.7 or Equation 3.8 in parentheses; rounded off LQL not in parentheses.

4.5 INCORPORATION OF WAD CYANIDE ANALYSIS TECHNIQUE INTO THE CYNOPROBE

Software and hardware changes were required to incorporate the analysis of WAD cyanide into the

Cynoprobe. These were completed by a team of engineers and instrument technicians. The sequence of operation was firstly to treat the plant filtrate with the ligand exchange reagent, to liberate WAD cyanide, before measuring the free cyanide concentration via amperometry in the Cynoprobe, as is illustrated in Figure 4.17.

Figure 4.17 Cynoprobe basic sequence of operation for free and WAD cyanide analysis in the same measurement cycle



Since the amperometric technique only detects CN^- ion and not $HCN_{(aq)}$, it is necessary to ensure that the pH of all solutions is 12, for WAD cyanide analysis. Though the basicity of the LEX reagent does increase the pH of mining filtrates to some extent, it is typically not sufficient for leach and residue filtrates with pH 9.5-10.5. It has therefore been necessary to dose sodium hydroxide and control the pH to 12. To recover all the free cyanide (CN^- and $HCN_{(aq)}$) the pH should also be adjusted to 12, however no adjustment is required to measure the actual cyanide available to leach gold. Since this is the preferred measurement for control purposes, except when high copper cyanide ratios are expected, the pH is not routinely adjusted to 12 for free cyanide measurement.

A dosing pump was required to pump the ligand exchage reagent and sodium hydroxide into the amperometric cell where it was agitated for 45-60 seconds, heated to the required set-point and finally analysed for 60 seconds.

The Cynoprobe may be configured to measure both free and WAD cyanide concentration either in the same or separate measurement cycles. A measurement cycle may be completed between 3-10 minutes, depending on the number of sampling streams, how far the sample has to be pumped, the set-point temperature and whether free and/or WAD cyanide is measured in the same or separate cycles. The fast analysis time, of approximately 5 minutes for only free or WAD analysis, makes the measurement suitable for use in control algorithms, such as those for cyanide addition and destruction.

Repetitive analysis showed that flushing the amperometric cell with plant filtrate a few times between measurements improves the accuracy of the WAD cyanide reading. Flushing possibly washes off any reagent that may have coated the working silver electrode.

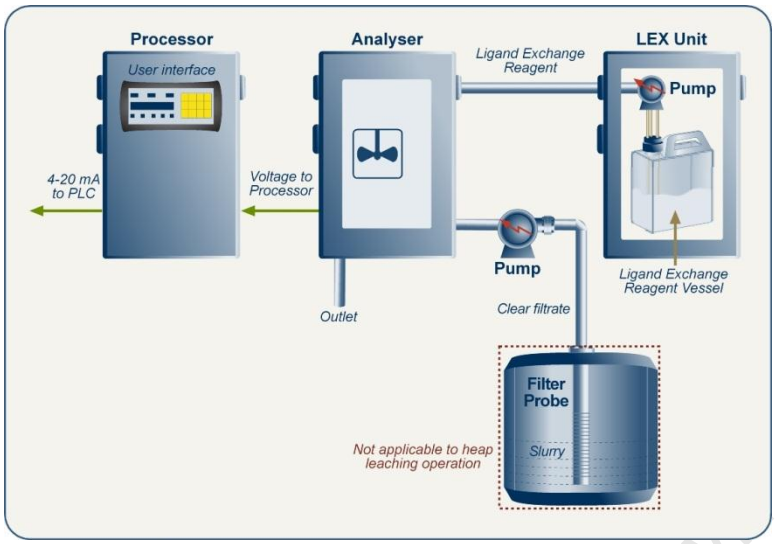
The 20% LEX reagent was stored in a sealed, dark 10 L vessel in order to avoid exposure to air and light.

The amperometric cell should be cleaned automatically approximately every 24 hours with two cleaning solutions; 3% hydrogen peroxide and 3% hydrochloric acid, respectively. Hydrochloric acid prevents the build up of lime and hydrogen peroxide being a strong oxidising agent is often used as a cleaning agent in many applications. The sequence of the cleaning cycle is firstly to clean with hydrogen peroxide, then hydrochloric acid and finally with hydrogen peroxide again so as to avoid acid coming into contact with cyanide.

The Cynoprobe prototype for online free and WAD cyanide analysis consisted of the following major hardware components, as shown in Figure 4.18.

- Filter Probe, inserted into a leach or residue tank to filter the slurry.
- Pump, to transport clear filtrate from the tank to the Cynoprobe for measurement.
- The Analyser Unit, for all the physical and chemical processes, containing the amperometric cell.
- The LEX Unit (Ligand Exchange Reagent Box), containing the reagent pump and vessel.
- The Processor Unit, containing all the electrical components.

Figure 4.18 **A schematic diagram showing various components of the Cynoprobe prototype for online free and WAD cyanide analysis**



4.6 CONCLUSION

An organic ligand exchange reagent was chosen based on its selectivity for copper, the most prevalent metal associated with gold that forms WAD cyanide, as well as its limited ability to bind with SAD cyanide metals; iron and cobalt. It was relatively inexpensive compared to other chelating reagents, not very hazardous, could be easily prepared by dilution and is readily available worldwide from chemical suppliers such as Merck, Sigma Aldrich and Huntsman international. For commercial reasons, Mintek required that the reagent's identity not be disclosed in this work.

The WAD cyanide measurement technique by ligand exchange with amperometric finish was optimised according to volume of ligand exchange reagent; 2 mL and 4 mL 20 % LEX reagent for normal and high base metal concentrations (<80 ppm and 300 ppm) respectively, and amperometric applied potential; -140 mV, to ensure no reaction between the working silver electrode and LEX reagent. Contact time and temperature were optimised to 5 minutes and 35ºC, respectively, for laboratory experiments. Though the liberation of cyanide appeared to be sensitive to temperature around 35ºC, the technique was otherwise found to be robust because of its insensitivity to contact time and temperature from 20-30ºC and 40-45ºC. The liberation of cyanide was not adversely affected by these two parameters and so adjustment to lower or higher temperatures, depending on location and season, should not adversely affect WAD cyanide recovery.

WAD cyanide recovery from pure copper, nickel, zinc and silver cyanide solutions, prepared from metal cyanide salts, with concentrations ranging from 0.5-100 ppm, were determined. Even though

the stability constants for the metal chelates indicated that the LEX reagent is most selective for copper, followed by nickel, zinc, cadmium, lead and silver (Section 4.1.3), average overall recoveries obtained in the laboratory indicated the following order of effectiveness; zinc (93.0%), copper (92.8%) and nickel (80.4%). Silver cyanide solutions could not be prepared from the pure salt as it is not commercially available. The solutions that were prepared from AgCN and NaCN consisted mostly of free cyanide and low quantities of aqueous silver cyanide. The stability constants for the metal cyanides, shown in Table 2.1 indicate that cyanide is weakly associated with zinc, moderately bound in the copper tri-cyanide complex by copper and most strongly bound to nickel. Since metal cyanide species are far more stable than the metal chelating complexes, the stability constants of the former determined the overall recoveries.

Initial and on-going WAD cyanide recovery from pure copper, zinc and silver cyanide solutions was 89-100% and 81-100% respectively. Initial and on-going recoveries from nickel cyanide were lower, 73-91% and 64-81%. Higher recoveries for nickel were obtained by increasing the volume of LEX reagent addition which according to Le Chatelier's principle shifts the chelation reaction equilibrium, promoting the liberation of cyanide, as shown in Section 4.3.1.3. Recoveries ranging from 83-130% for 10-100 ppm WAD CN were obtained from 6 mL 10% LEX reagent. Even higher recoveries were obtained for higher LEX reagent concentrations.

WAD cyanide recoveries were also determined by analysing a synthetic representative of a real plant solution consisting of 40% free cyanide, 40% copper cyanide and 20% nickel cyanide. Initial and on-going accuracy and precision was 92-98% (<6.9% RSD) and 83-96% (<8% RSD).

Table 4.17 below shows the initial and on-going accuracy and precision data obtained for the Cynoprobe's WAD cyanide reading, as compared to the quality control acceptance criteria of laboratory standard test methods. Recoveries from both the pure and combination metal cyanide standards fall within the recovery range of ASTM D-6888-04. The initial and on-going accuracy and precision data for the combination standard solution fall within Method OI-1677's criteria, except for the initial recovery which is 1% less. However, the initial and on-going percent recoveries for the pure metal cyanide standards are slightly less than the range specified by Method OI-1677, by 1-4%. Such recoveries could be expected considering the concentration mark-up of the respective maximum concentrations for the laboratory methods and Cynoprobe, 400 ppb and 100 ppm respectively, as well as the exclusion of a matrix separation step in the Cynoprobe. The Cynoprobe's initial accuracy and precision for laboratory standard solutions was therefore 12% error and 9% RSD respectively. Since real plant solutions are expected to contain metal concentrations less than those present in standard solutions prepared from metal cyanide salts, the required

accuracy of ±10% for industrial implementation was envisaged to be achievable, but needed to be proven onsite.

Table 4.17 Initial and on-going accuracy and precision data for Cynoprobe WAD cyanide measurement, compared to standard test methods

Method	Initial recovery and RSD	On-going recovery and RSD
Cynoprobe (Pure Me-CN solns)	89-100% (<8.5%)	81-100% (<4.5%)
Cynoprobe (Comb Me-CN solns)	92-98% (<6.9%)	83-96% (<8%)
Method OI-1677	92-122% (<5.1%)	82-132% (<11%)
ASTM D-6888-04	70-114% (<11.1%)	-

Values are percent recoveries; values in parentheses are percent relative standard deviations.

CHAPTER FIVE

Instrument refinements to accommodate more complex ore types

5.0 COMPLEX AND REFRACTORY ORES

The world's gold ore reserves with simple metallurgy are running out and a trend has emerged in the gold mining industry where refractory and complex ore is being mined. Refractory ore refers to ore where gold is difficult to extract. This may either be because it is physically or chemically locked in a host mineral or associated with minerals that consume cyanide and/or oxygen. Physical refractoriness can be overcome by ultra-fine grinding (microcrystalline quartz and silicates). However, chemical refractoriness requires the oxidation of the host mineral, such as pyrite (FeS_2), arsenopyrite (FeAsS) and pyrrhotite (Fe_7S_8), to obtain economical gold recoveries. Examples of pre-treatment technologies include pressure oxidation (POX) with an autoclave, roasting and the BIOX® process. Carbonaceous material and other complex ores containing copper such as chalcocite (Cu_2S) result in excess cyanide consumption (Gold Metallurgy, 2012; Marsden and House, 1992).

The cyanidation of more complex ores results in a variety of species forming in solution, such as sulphide, intermediate oxidised sulphur species and cuprous cyanide compounds. Sulphur species such as sulphide, thiosulphate and thiocyanate often result in interferences. The impact of copper cyanides and sulphur species on the Cynoprobe's amperometric response was investigated.

5.1 SULPHIDE MINERALS

Pyrite, chalcopyrite, chalcocite, bornite, pyrrhotite and arsenopyrite are the main sulphide minerals locking gold in refractory sulphide gold ores. Most metal sulphides decompose in aerated, alkaline cyanide solution to form various sulphur-containing species including thiocyanate, sulphide and thiosulfate ions, with polythionates and polysulfides having also been detected (Marsden and House, 1992). During cyanidation, the pulp is aerated to facilitate the formation of thiosulphate and sulphate instead of thiocyanate and prevent further cyanide consumption. Other intermediate oxidised sulphur species such as dithionate ($S_2O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$) and pyrosulphate ($S_2O_7^{2-}$) may form under various conditions (Hewitt *et al.*, 2009).

5.1.1 Blank sample analysis with sulphur species

The following likely interferent additions were selected for analysis with the Cynoprobe:

- Sulphide (S^{2-})
- Thiocyanate (SCN^{-})
- Thiosulphate ($S_2O_3^{2-}$)
- Sulphite (SO_3^{2-})
- Dithionate ($S_2O_6^{2-}$)
- Tetrathionate ($S_4O_6^{2-}$)
- Pyrosulphate ($S_2O_7^{2-}$)
- Sulphate (SO_4^{2-})

Cynoprobe v2.0, using the potentiostat board v2.0 (4020 Ω resistor, 0.4-30 ppm CN) with an applied voltage of 0 mV was calibrated with four sodium cyanide standard solutions (0.4, 5, 15, 30 ppm) and tap water at 35ºC.

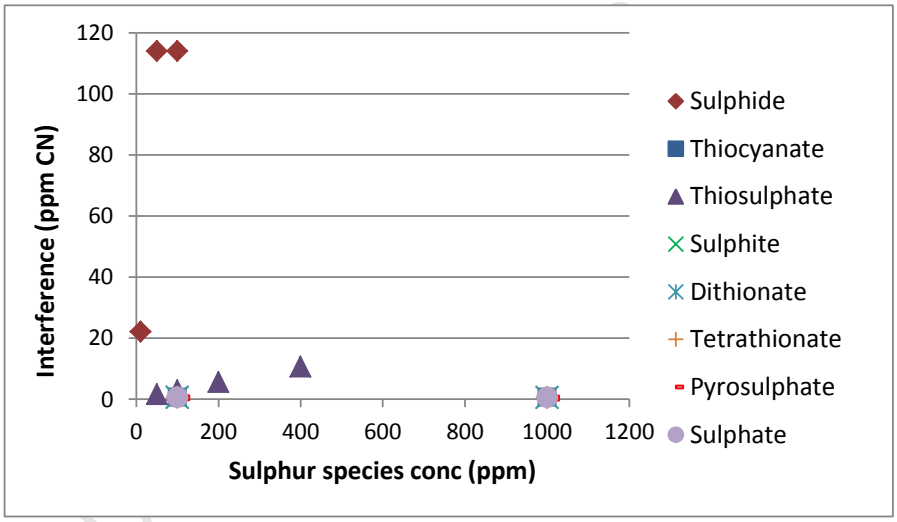
Blank solutions, containing no cyanide in solution were analysed in the Cynoprobe to test for interference from sulphur species. Table 5.1 shows the species concentrations and the amperometric response concentrations (as cyanide), together with the percent relative standard deviation, obtained from five readings. No real interference from thiocyanate, sulphite, dithionate, tetrathionate, pyrosulphate and sulphate was observed. For both 100 and 1000 ppm the average concentrations were <0.8 ppm, close to the quantification limit of 0.4 ppm for 4020 Ω. However, the presence of both sulphide and thiosulphate resulted in false positive free cyanide analysis. Low concentrations of sulphide, 10 ppm S_2^{-} produced interference equivalent to 22.14 ppm CN. The interference increased proportionately to 114.00 ppm for 50 ppm S_2^{-}, but plateaued out at this concentration (Figure 5.1). At this point the working silver electrode appeared to be completely covered by black silver sulphide. Thiosulphate interference increased proportionately with increasing concentration. It produced analytical signals equivalent to approximately 2, 3, 6 and 11 ppm CN for 50, 100, 200 and 400 ppm $S_2O_3^{2-}$.

Table 5.1 **Average concentrations and relative standard deviation from the blank analysis of sulphur species in the Cynoprobe (4020 Ω, 35ºC, V_{sp} = 0 mV)**

Concentration (ppm)	Cynoprobe amperometric response (ppm CN)							
	S^{2-}	SCN^{-}	$S_2O_3^{2-}$	SO_3^{2-}	$S_2O_6^{2-}$	$S_4O_6^{2-}$	$S_2O_7^{2-}$	SO_4^{2-}
10	22.14 (0.5%)	-	-	-	-	-	-	-
50	114.00 (0.0%)	-	1.61 (0.85%)	-	-	-	-	-
100	114.00 (0.0%)	0.71 (0.7%)	2.93 (1.5%)	0.61 (1.1%)	0.62 (1.1%)	0.66 (2.0%)	0.45 (6.2%)	0.62 (0.9%)
200	-	-	5.65 (0.5%)	-	-	-	-	-
400	-	-	10.66 (2.6%)	-	-	-	-	-
1000	-	0.70 (0.73%)	-	0.55 (2.3%)	0.57 (2.9%)	0.60 (1.9%)	0.39 (0.9%)	0.62 (1.6%)

Values are an average of five readings; numbers in parentheses are percent relative standard deviations.

Figure 5.1 **Blank analysis of sulphur species in the Cynoprobe (4020 Ω, 35ºC, V_{sp} = 0 mV)**



5.1.2 Combination metal cyanide solution analysis with sulphur species

No interference was observed during the blank sample analysis of thiocyanate, sulphite, dithionate, tetrathionate, pyrosulphate and sulphate. However, sulphide and thiosulphate species were found to produce a false analytical signal at an applied potential of 0 mV. Sulphide, thiocyanate, thiosulphate and sulphate are the most common sulphur species found in gold mining solutions. Interference tests from these species in metal cyanide solutions were therefore performed.

Cynoprobe v2.0, using the potentiostat board v2.0 (1214 Ω resistor, 10-100 ppm CN) with an applied voltage of 0 mV was calibrated with four sodium cyanide standard solutions (10, 20, 50, 100

ppm) and tap water at 35ºC.

Sulphur salts were added to combination metal cyanide solutions consisting of 40% free cyanide, 40% copper cyanide and 20% nickel cyanide at concentrations 10, 50 and 100 ppm WAD CN. The solutions were analysed in triplicate without LEX reagent addition, for free cyanide, and the average concentrations, together with the percent relative standard deviations are shown in Table 5.2.

Table 5.2 **Average concentrations and relative standard deviation from the free cyanide analysis of WAD cyanide solutions in the presence of sulphur species in the Cynoprobe (1214 Ω, 35ºC, V_{sp} = 0 mV)**

Concentration (ppm WAD CN)	Blank (no LEX reagent)	SCN^-	SO_4^{2-}	S^{2-}		$S_2O_3^{2-}$	
		100 ppm	100 ppm	1 ppm	10 ppm	10 ppm	100 ppm
10	6.48	6.40 (1.3%)	6.21 (0.7%)	10.06 (2.2%)	27.72 (7.0%)	6.39 (0.4%)	12.67 (1.0%)
50	25.88	26.01 (1.1%)	24.81 (1.9%)	28.87 (1.6%)	47.39 (0.6%)	26.07 (0.4%)	32.34 (1.2%)
100	50.24	49.38 (1.3%)	51.33 (2.3%)	54.40 (0.5%)	73.32 (1.0%)	51.51 (1.4%)	60.31 (0.6%)

Values are an average of three readings; numbers in parentheses are percent relative standard deviations.

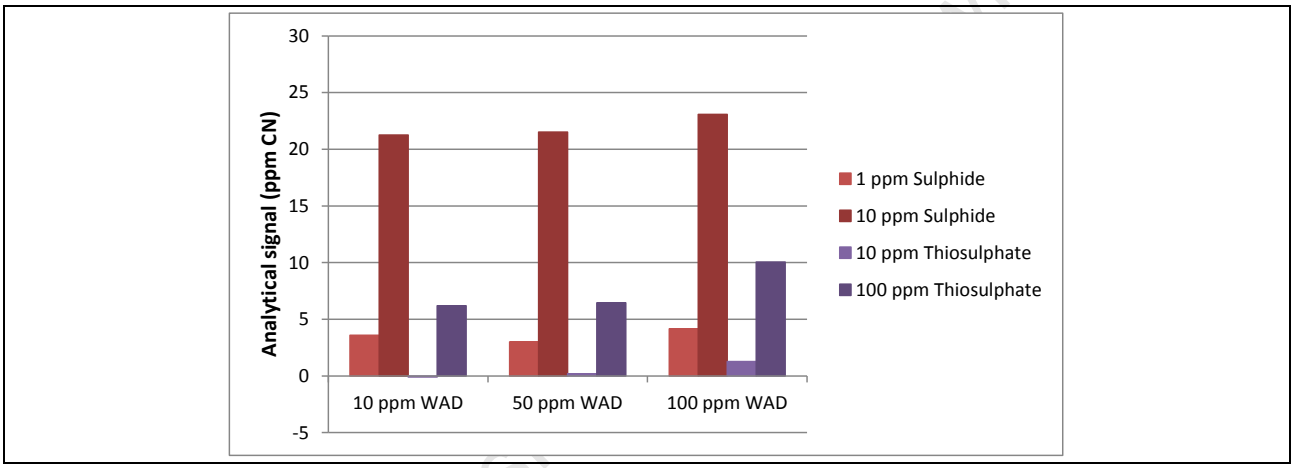
Table 5.3 shows the interference and percent deviation (average from actual) for each data set. As was the case for the blank samples, no interference from 100 ppm thiocyanate and sulphate was observed. Positive and negative differences from the actual concentration were less than 1.1 ppm (<5% deviation), within the instrument error of 5% for free cyanide analysis. Sulphide and thiosulphate produced positive interferences, the former the most severe. As was the case for blank solutions, 10 ppm sulphide induced an analytical signal equivalent to ~22 ppm. 100 ppm thiosulphate produced a greater interference in WAD cyanide solutions of 6-10 ppm, compared to the blank result of 3 ppm. Higher concentrations of free cyanide may be present in solution as a result of the formation to metal thiosulphate species. As can be seen in Figure 5.2, sulphide and thiosulphate interference was independent of WAD cyanide concentration for 10 and 50 ppm WAD CN. An increase of interference was noticed for 100 ppm WAD CN, but was possibly due to re-speciation from the formation of metal sulphides and thiosulphates.

Table 5.3 **Interference and deviation from the free cyanide analysis of WAD cyanide solutions in the presence of sulphur species in the Cynoprobe (1214 Ω, 35ºC, V_{sp} = 0 mV)**

Concentration (ppm WAD CN)	SCN^-	SO_4^{2-}	S^{2-}		$S_2O_3^{2-}$	
	100 ppm	100 ppm	1 ppm	10 ppm	10 ppm	100 ppm
10	-0.08 (1.2%)	-0.27 (4.1%)	3.59 (55.4%)	21.25 (328.1%)	-0.09 (1.3%)	6.20 (95.7%)
50	0.14 (0.5%)	-1.07 (4.1%)	3.00 (11.6%)	21.51 (83.1%)	0.19 (0.7%)	6.46 (25.0%)
100	-0.87 (1.7%)	1.09 (2.2%)	4.15 (8.3%)	23.08 (45.9%)	1.27 (2.5%)	10.06 (20.0%)

Values are interferences; numbers in parentheses are deviations (average from actual).

Figure 5.2 **Sulphide and thiosulphate interferences to the analytical signal of Cynoprobe (1214 Ω, 35ºC, V_{sp} = 0 mV)**



5.1.3 Interference from sulphide and thiosulphate

Sulphide is typically not present in leach slurries or tails. However it may be present at the start of the leach of very sulphidic ores or in the residue where biological destruction of thiocyanate is employed, in concentrations <10 ppm (concentrations escalate in poorly aerated slurries or solutions). Should the Cynoprobe be sampling the head tank for cyanide addition control or the residue for biological destruction control, the interference from sulphide would need to be removed.

Thiosulphate concentrations can vary between 200 and 600 ppm in real gold mining solutions of sulphidic ores. It was therefore necessary to find a solution to remove such interferences from the Cynoprobe's cyanide measurement.

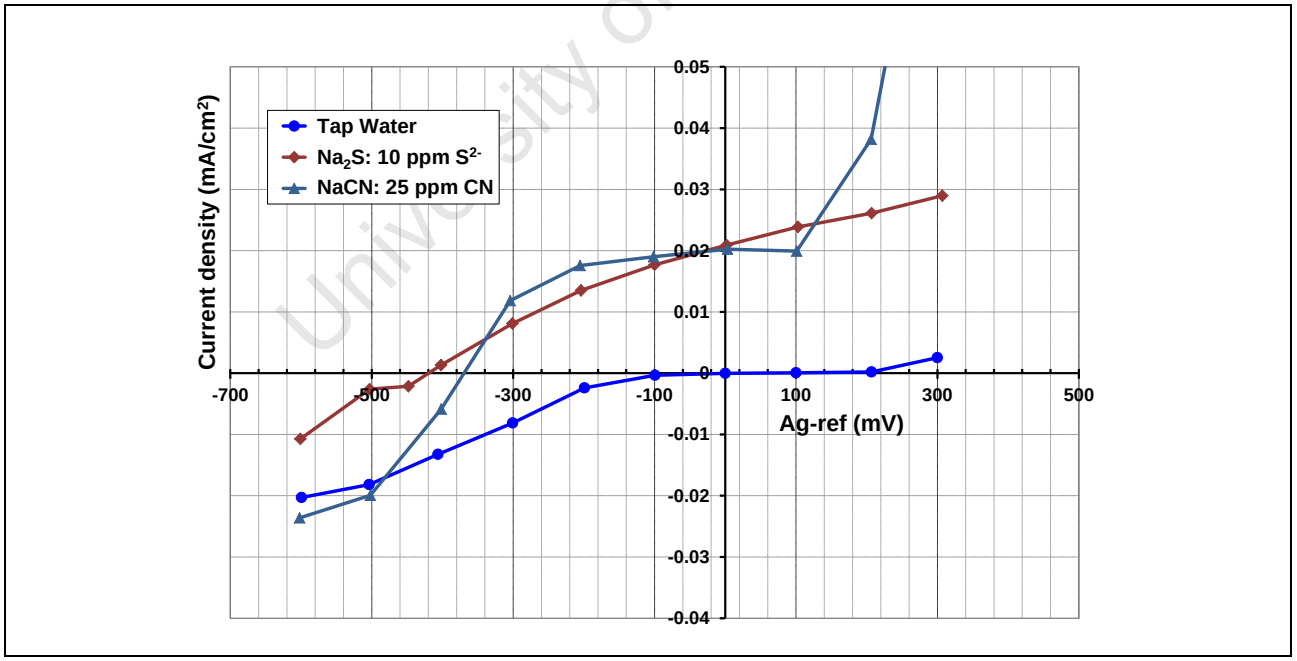
5.1.3.1 Voltammograms for sulphide and thiosulphate

Single-potential amperometry has been used to detect weak acid anions, such as cyanide and sulphide, as well as other ions, such as iodide, sulphite, and hydrazine. An advantage of amperometry over other detection methods is specificity; the applied potential can be adjusted to maximize the response for the analyte of interest while minimizing the response for interfering analytes (Settle, 1997). Voltammograms for sulphide and thiosulphate were generated in order to understand the behaviour of these species at different applied potentials.

5.1.3.1.1 Voltammograms for blank sulphide solutions

Figure 5.3 below shows the voltammogram for 10 ppm sulphide, compared to 25 ppm CN. The current density for 10 ppm sulphide at 0 mV of 0.02 mA/cm^2 is equivalent to a detection of 25 ppm CN. Both curves have a similar steady state region. Sulphide begins to react with silver at a lower applied potential than cyanide does, (-425 mV and -355 mV respectively). Therefore, removing sulphide interference by adjusting the applied potential would not be feasible.

Figure 5.3 Cynoprobe voltammograms for sulphide in water (4020 Ω, 35ºC, cylindrical silver electrode)



5.1.3.1.2 Voltammograms for blank thiosulphate solutions

Figure 5.4 shows the voltammograms for blank thiosulphate solutions; 100 and 400 ppm $S_2O_3^{2-}$ in water for a cylindrical silver electrode. According to Table 5.4, 100 and 400 ppm thiosulphate begin

to react with silver at an applied potential of -150 and -200 mV respectively. The current density appeared to increase almost exponentially with increase in applied potential for 400 ppm thiosulphate. Thiosulphate interference at 0 mV is proportionate to concentration. Applying a voltage of approximately -150 mV will ensure that thiosulphate does not react with the silver electrode.

Figure 5.4 **Cynoprobe voltammograms for thiosulphate in water (4020 Ω, 35ºC, cylindrical silver electrode)**

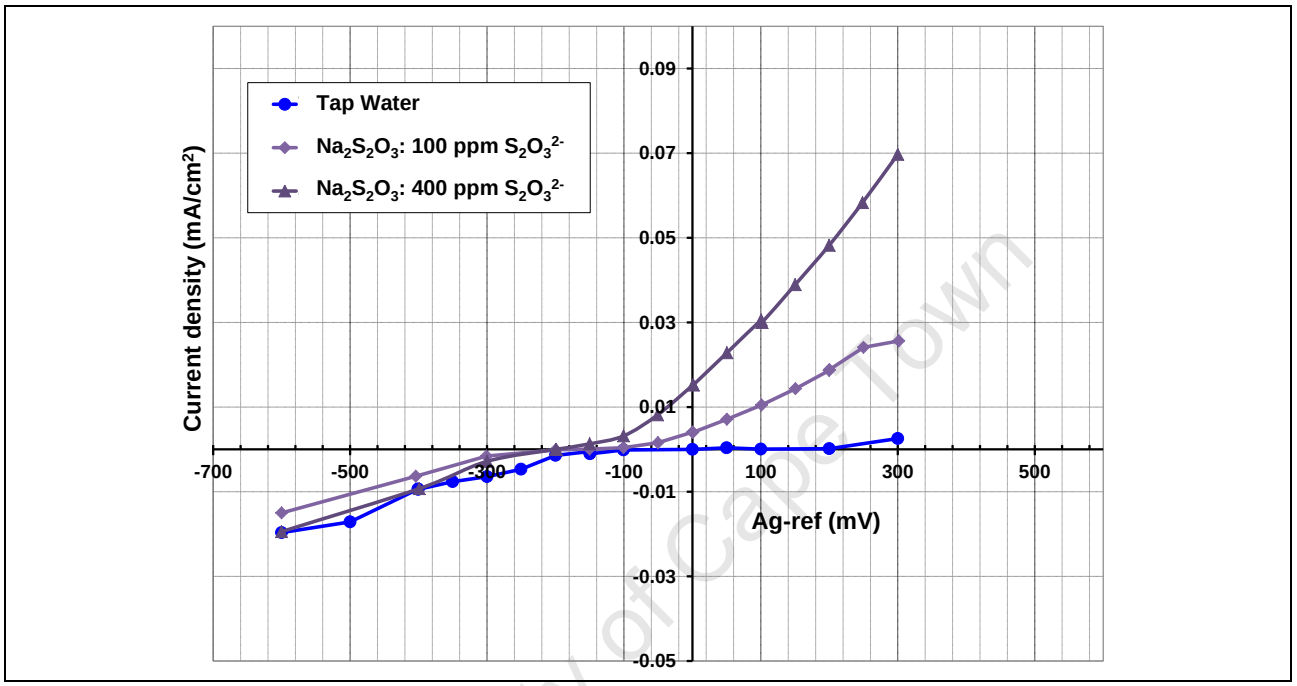


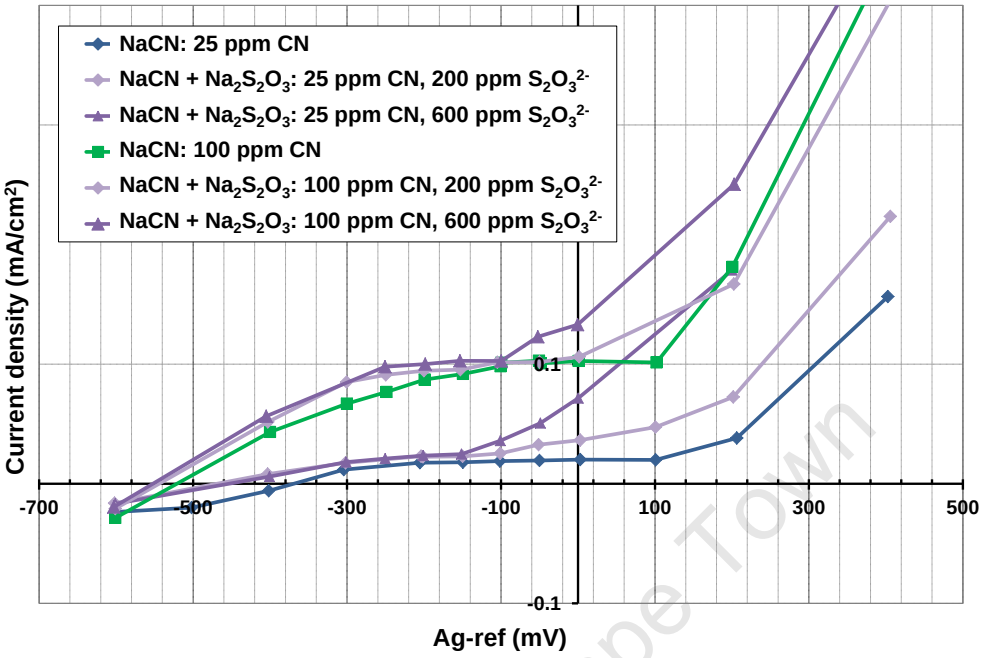
Table 5.4 **Applied potential and resulting current densities for 100 and 400 ppm thiosulphate, close to the point of no interference (zero current)**

Set-point voltage (mV)	Resulting current density (mA/cm^2)	
	100 ppm $S_2O_3^{2-}$	400 ppm $S_2O_3^{2-}$
-400	-6.34E-03	-9.27E-03
-300	-1.58E-03	-2.83E-03
-200	-9.33E-05	5.87E-06
-150	7.10E-05	5.87E-06
-100	3.87E-04	3.19E-03
-50	1.58E-03	8.16E-03
0	4.06E-03	1.53E-02

5.1.3.1.3 Voltammograms for cyanide and thiosulphate solutions

Low and high concentrations of sodium cyanide (25 ppm and 100 ppm CN) were mixed with both low and high concentrations of thiosulphate (200 ppm and 600 ppm $S_2O_3^{2-}$). Figure 5.5 shows the voltammetric curves for the various mixes for a hemispherical silver electrode.

Figure 5.5 **Cynoprobe voltammograms for thiosulphate in sodium cyanide solutions (40.75 Ω, 35ºC, cylindrical silver electrode)**



The resulting current densities for each solution, together with the interferences are shown in Table 5.5. The interference from 200 ppm and 600 ppm thiosulphate became evident at -140 mV and higher. Moreover, higher thiosulphate concentrations showed higher interference. Therefore, slightly lower applied potentials are necessary to remove higher thiosulphate concentrations. For cyanide solutions, a voltage set-point of -150 mV will remove interference from up to 600 ppm thiosulphate.

Table 5.5 **Applied potential and resulting currents for 25 ppm CN with thiosulphate 200 and 600 ppm thiosulphate, close to zero interference**

Set-point voltage (mV)	Resulting current density(mA/cm^2)		
	25 ppm CN	25 ppm CN, 200 ppm $S_2O_3^{2-}$	25 ppm CN, 600 ppm $S_2O_3^{2-}$
-200	0.0176	0.0230 (0.005)	0.0235 (0.006)
-150	0.0179	0.0229 (0.005)	0.0248 (0.007)
-100	0.0190	0.0253 (0.006)	0.0360 (0.017)
-50	0.0195	0.0326 (0.013)	0.0507 (0.031)
0	0.0202	0.0365 (0.016)	0.0716 (0.051)

Values are resulting current densities; numbers in parentheses are interference current densities (thiosulphate solution from cyanide solution).

5.1.3.2 Removal of sulphide interference

Sulphide readily reacts with Pb(II) ions to form insoluble lead sulphide. Sulphide may therefore be precipitated out of solution as lead sulphide. The addition of lead ions followed by filtering is a standard method for removing interference of sulphide ions for silver nitrate titration (Breuer and Rumball, 2007). A well-known example of a water soluble lead compound is lead acetate. Therefore, lead acetate may be dosed to the Cynoprobe cell prior to measurement.

5.1.3.2.1 Laboratory experiments

Experiments were performed in order to investigate the removal of sulphide interference from blank and cyanide solutions by the addition of lead acetate. Table 5.6 below shows that for clean water and cyanide solutions, lead acetate suppresses the Cynoprobe counts reading slightly. Therefore, the Cynoprobe was calibrated in the presence of lead acetate with potentiostat board v2.0 (1214 Ω, 10-100 ppm CN, -148.2 mV) at 35ºC. 2 mL 5500 ppm lead acetate solution was added to the Cynoprobe cell prior to measurement (approximate 1:1 molar ratio between lead acetate and <10 ppm sulphide in 100 mL). Negative counts are sometimes obtained for water when the instrument is set up with a negative voltage set-point.

Table 5.6 Cynoprobe counts without and with 2 mL 5500 ppm lead acetate addition (1214 Ω, -148.2 mV)

Calibration standard	Without lead acetate		With lead acetate	
	Counts	Concentration (ppm CN)	Counts	Concentration (ppm CN)
Water	-659	0	-1149	0
50 ppm	11177	50.98	10183	47.39
100 ppm	21612	97.41	21513	95.30

Sulphide was added to sodium cyanide solutions in the form of sodium sulphide. Table 5.7 below shows the cyanide concentrations obtained before and after lead acetate addition (2 mL 5500 ppm per 100 mL solution). The Cynoprobe was configured to measure free and WAD cyanide; the WAD cyanide cycle included the addition of LEX reagent.

The first set of experiments was performed for free cyanide measurement alone. Approximately 5 and 10 ppm sulphide produced interferences equivalent to 10 and 20 ppm CN, respectively in sodium cyanide solutions at pH 10.2 (mimicking the pH of gold leach solutions). After lead acetate addition to the amperometric cell, a dark brown lead sulphide precipitate became evident and

settled out before measurement. At pH 10, the interference was removed. However, at pH 12, 4 and 20 ppm interference from 1 and 10 ppm sulphide respectively, was not removed by the addition of lead acetate. Lead sulphide hydrolyses at pH >11.5 and it was noticed that after about half an hour the brown precipitate was no longer visible in solutions at pH 12. Since the pH of mining solutions is very rarely 12 and typically ranges between 10 and 11.5, interference from ≤10 ppm sulphide may be removed from the Cynoprobe's free cyanide reading by the addition of lead acetate.

For the second set of experiments the WAD-only function was enabled in the Cynoprobe, so that 4 mL 20% LEX reagent was dosed into the cell after lead acetate addition. Under these conditions, interferences equivalent to 5, 10 and 20 ppm CN from 1, 5 and 10 ppm sulphide were not completely removed. When the LEX reagent was added the cloudiness in the solution disappeared almost instantly and the solution became a clear brown colour. Over time the solution became less brown. This indicated that in the presence of the LEX reagent sulphide re-dissolved and the interference returned. To avoid the re-dissolution of sulphide the solution was filtered to remove lead sulphide before LEX reagent addition. In this case, interference of 10 ppm sulphide in the presence of 96.66 ppm sodium cyanide was removed. Therefore, precipitation of lead sulphide followed by a filtering step would be required to remove sulphide interference from the Cynoprobe's WAD cyanide measurement.

Finally, the Cynoprobe was configured to measure both free and WAD cyanide consecutively. Approximately 20 ppm interference due to 10 ppm sulphide in 81.53 ppm sodium cyanide solution was removed from the free cyanide measurement by lead acetate addition. However, after a few measurements interference was observed again. According to X-ray fluorescence (XRF) analysis the electrode was coated with lead sulphide. Lead has a great affinity for all precious metals, and so will readily bind with silver. It is likely that the LEX reagent reacted with PbS on the silver electrode, dissolved it and produced an 'additional' current. The electrode was then cleaned with steel wool and the solution filtered before analysis with LEX reagent. Under these conditions interference was removed. Therefore, to remove sulphide interference from consecutive measurement of free and WAD cyanide, the electrode should be cleaned with nitric acid to remove lead and the solution should be filtered before LEX reagent addition.

Table 5.7 Removal of sulphide interference by addition of lead acetate (2 mL 5500 ppm lead acetate) to sodium cyanide solutions at pH 10.2

Cynoprobe configuration	Clean NaCN solution (ppm CN)	pH	Sulphide addition (ppm S^{2-} in Cynoprobe cell)	NaCN solution with sulphide interference (ppm CN)	After lead acetate addition (ppm CN)
Free CN	32.18	12.0	1	36.99	36.03
	40.55	12.0	1	44.22	43.22
	50.49	12.0	10	69.68	73.57
	63.50	10.2	5	72.02	64.12
	90.89	10.2	10	109.60	91.46
WAD CN (with LEX reagent)	1.62 [T]	11.2	1	7.17 [T]	8.48 [T]
	73.06 [T]	11.2	5	86.64 [T]	83.49 [T]
	103.37 [T]	11.2	10	118.01 [T]	111.89 [T]
	77.55 [T]	11.1	10	97.16 [T]	101.75 [T]
	96.66 [T]	11.2	10	119.67 [T]	95.56 [F, T]
Free & WAD CN	81.53	10.1	10	100.42 111.59 [T]	82.37 111.20 [T] 78.35 [S, F, T]

[F] Filtered. [T] 4 mL 20% LEX reagent addition. [S] Electrode manually cleaned with steel wool.

The above experiments showed that a filtering step would be required to measure WAD cyanide and a nitric acid cleaning step would be required for consecutive free and WAD cyanide measurement. Both these steps would be impractical to implement. As yet, they have not been required, since sulphide has not been reported to be present at the typical WAD cyanide analysis points, post leach or before discharge.

5.1.3.2.2 Plant set up

5.1.3.2.2.1 Testing for the presence of sulphide

Lead acetate test strips (paper previously moistened with acetate buffer) may be used to detect 50 ppm or more sulphide in plant filtrate to be analysed in the Cynoprobe. The paper will turn brown to black depending on the concentration of sulphide in solution. Lead acetate powder should be used to detect lower sulphide concentrations. A brown cloud in solution after the addition of the powder is evidence of sulphide.

5.1.3.2.2.2 Large sulphide concentrations (>10 ppm)

If lead acetate is added to remove large concentrations of sulphide (>10 ppm), the pH decreases due to the excess lead hydrolysis and precipitation as PbO. This results in some $HCN_{(aq)}$ forming, which is not measured in the case of the Cynoprobe. To avoid this, the pH in the cell should be controlled with sodium hydroxide addition (Breuer and Rumball, 2007). Lead carbonate does not decrease the pH (ASTM D-6888-04). Therefore, if the sulphide concentration is very high, lead carbonate may be added to avoid reducing the pH significantly.

5.1.3.2.2.3 Lead acetate or lead carbonate addition

Sulphide in concentrations of less than 10 ppm are most likely to be present in solutions where free cyanide is measured, especially at the start of the leach. In this case, an additional dosing pump will be installed and the software configured to dose 2 mL 6000 ppm (pH 9-10) lead acetate to the cell after filling with filtrate. Should larger concentrations be present, the lead acetate solution will be prepared to a slightly more alkaline pH and the pH controlled in the cell, or lead carbonate should be added (concentration prepared according to the quantity of sulphide to be removed).

5.1.3.3 Removal of thiosulphate interference

According to the voltammograms for thiosulphate in cyanide solutions, applying a voltage of approximately -150 mV will ensure that up to 600 ppm thiosulphate does not react with the silver electrode. Should the Cynoprobe be required to measure cyanide in plant filtrate containing thiosulphate, the voltage set-point of potentiostat board v2.0 should be tweaked according to the maximum thiosulphate concentration present in solution.

5.2 COPPER MINERALS

Since copper is the most common base metal associated with gold, WAD cyanide recoveries from all three copper cyanide complexes $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$ were determined by analysing copper cyanide solutions with excess and starved of cyanide. The likelihood of copper plating out on the working silver electrode and resulting in interferences was investigated by comparing copper and silver cyanide voltammograms.

5.2.1 WAD cyanide recovery from copper cyanide species

WAD Cyanide recoveries from copper cyanide species in the Cynoprobe were also determined. Copper cyanide solutions with excess and starved of free cyanide were prepared in order to obtain $[Cu(CN)_4]^{3-}$, $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_2]^{-}$ in solution. Two copper cyanide standards with 63 ppm (1 mmol/L) copper and Cu:CN molar ratios of 1:7 and 1:2.5 were prepared at pH 12 and 9.31 respectively. Table 5.8 below shows the theoretical speciation of the standards as predicted by Mintek speciation spread-sheet. The stability of $[Cu(CN)_3]^{2-}$ is once again highlighted by high equilibrium concentrations in all solutions. Solutions with higher free cyanide concentrations, with a Cu:CN molar ratio of 1:7 show the increased likelihood of $[Cu(CN)_4]^{3-}$ being present in solution. Nearly equal quantities of $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_2]^{-}$ are predicted for solutions starved of free cyanide with a Cu:CN molar ratio of 1:2.5.

The Cynoprobe was calibrated with potentiostat board v1.0 at 555.6 Ω (10-200 ppm CN). 2 mL 20% LEX reagent was added to the amperometric cell before WAD cyanide measurement. Table 5.8 below also shows the Cynoprobe's WAD cyanide concentration obtained from an average of at least five readings. The WAD cyanide recoveries for solutions with a Cu:CN molar ratio of 1:7 at pH 12 and 9.31 was close to 100%, indicating excellent recoveries from $[Cu(CN)_4]^{3-}$ and $[Cu(CN)_3]^{2-}$. The WAD cyanide recoveries for solutions with a Cu:CN molar ratio of 1:2.5 at pH 12 and 9.31 were 78.5% and 100.5% respectively. Solutions with low Cu:CN molar ratios were difficult to prepare as CuCN did not dissolve easily. This could be the reason for the under-recovery at pH 12 for this solution. Nevertheless the excellent results overall indicated that the Cynoprobe's ligand exchange technique with amperometric finish recovers WAD cyanide from the three copper-cyano species.

An intense turquoise blue colour was visible after the addition of the ligand exchange reagent to the solutions. The blue colour is indication of the tetra-amine Cu(II) chromophore (Wikipedia, 2012) and hence is an indication of the ligand exchange reaction.

Table 5.8 **Cyanide speciation and WAD cyanide recovery from copper cyanide standards with 63 ppm (1 mmol/L) copper and high and low free cyanide concentrations at pH 12 and 9.31**

Species	Concentration (ppm)			
	Cu:CN 1:7		Cu:CN 1:2.5	
	pH 12.00	pH 9.31	pH 12.00	pH 9.31
CN^-	100.00	50.4	0.14	0.13
$HCN_{(aq)}$	0.16	50.40	0.00	0.13
$[Cu(CN)_2]^-$	0.10	0.21	30.92	31.20
$[Cu(CN)_3]^{2-}$	73.61	75.18	30.94	30.52
$[Cu(CN)_4]^{3-}$	4.75	2.45	0.00	0.00
Free CN	100.20	100.80	0.14	0.27
WAD CN	178.60	178.60	62.00	62.00
Cynoprobe	176.25 (1.0%)	178.70 (1.8%)	48.67 (10.2%)	62.30 (5.9%)
Percent recovery	98.7%	100.0%	78.5%	100.5%

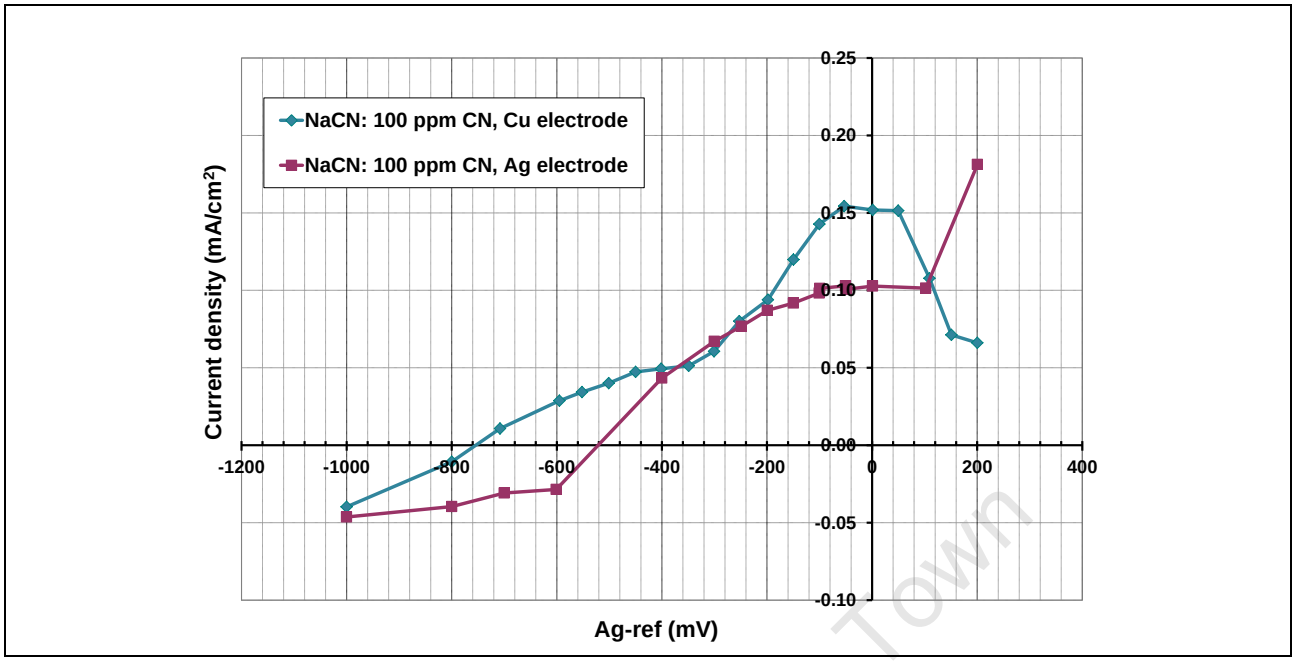
Cynoprobe values are average readings; numbers in parentheses are percent relative standard deviations.

5.2.2 Copper plating on silver electrode

5.2.2.1 Cyanide voltammograms for copper and silver electrodes

On a number of plants a coppery coloured deposit was observed on the silver electrode that was suspected to be copper. The likelihood of copper plating on the silver electrode was investigated by plotting cyanide voltammograms for silver and copper electrodes. Figure 5.6 shows the voltammograms of hemispherical copper and silver electrodes in cyanide. The stability of copper cyanide complexes to silver cyanide complexes may be compared. It is clear that the copper cyanide reaction is initiated at more negative voltages than the silver cyanide reaction does. At the Cynoprobe's typical set-point voltage copper will prefer to stay in solution and not plate out on the silver electrode (assuming an even distribution of current density on the silver electrode).

Figure 5.6 **Voltammograms for 12 mm diameter hemispherical Cu and Ag electrodes (354.2 Ω, 35ºC)**



5.2.2.1.1 Stripping phase in cleaning cycle

A stripping phase was introduced to the cleaning cycle in order to remove unknown and unwanted deposits. A negative voltage of approximately -1000 mV was applied for a few seconds during the hydrochloric acid cleaning phase and proved to be effective in stripping the electrode of all deposits. When implemented at a gold plant where gypsum deposits were problematic, it was found that a negative voltage of -1000 mV applied during the automatic cleaning cycle every day did maintain the silver electrode as required.

5.3 HIGHLY SALINE PROCESS WATER

Much of Australia's landscape is naturally saline. Over millions of years, salt from what was ocean, was carried inland by wind and rain to form large salt deposits. Other sources of salt include inland seas that evaporated and the weathering of parent rocks that were formed with salt. These salt deposits were predominantly held deep within the soil profile but farming practices and rising water tables have brought the salt to the surface. Salinity is classified as a dissolved salt content of a substance like soil or water. Dry land salinity (occurring on land not subject to irrigation) currently affects more than 5 million hectares of land, mostly in southern Australia. Western Australia, in particular, is known for high salinity levels. Total Dissolved Salts (TDS) values in the groundwater typically range from 50,000 – 150,000 ppm, depending on the time of the year and are mainly due to chloride and sodium ions. Other anions and cations that may be present in smaller quantities are

nitrate, sulphate and potassium ions (Australian Academy of Science, 2012).

5.3.1 Chloride levels in Australian leach and tails samples

Process mining waters of many gold plants in Australia are therefore characterised by high salinity levels. Leach and tails samples from five mines in Australia were analysed at Mintek for chloride by silver nitrate titration Table 5.9 below shows the pH, conductivity and redox potential of the samples. Chloride levels ranged from 150-70 000 ppm. The highly saline samples also showed high conductivities ranging from 20-65 $mS.cm^{-1}$ and reducing (negative) potentials.

Table 5.9 Analysis of highly saline leach and tails samples from Australia

Gold plant sample	pH	Redox potential (mV)	Conductivity ($mS.cm^{-1}$)	Chloride concentration. (g/L)
Plant 1 Sample 1	9.68	27	1.40	0.89
Plant 1 Sample 2	9.78	55	1.69	0.20
Plant 1 Sample 3	9.78	55	1.69	0.22
Plant 2 Sample 1	11.65	-104	4.79	0.15
Plant 2 Sample 2	11.75	-121	4.01	0.20
Plant 3 Leach Feed	9.72	3	65.85	32.10
Plant 3 Tail	9.35	118	61.70	30.40
Plant 4 Leach Tank 2	12.51	-135	60.20	70.20
Plant 4 Leach Tank 7	12.16	-85	23.55	69.10
Plant 5 Leach Tank 1	12.1	-83	56.55	26.65
Plant 5 Tail	12.33	-111	33.75	27.30

5.3.2 Cynoprobe voltammograms for chloride solutions

Since Australian gold plants showed interest in the Cynoprobe, the effect of salinity on the instrument's cyanide measurement had to be investigated. In so doing hardware modifications had to be made also, which are beyond the scope of this thesis.

Figure 5.7 shows the voltammetric curve of the silver electrode in sodium chloride solution. Comparing the voltammograms for chloride and tap water; whereas the current density for tap water remained close to zero as the applied potential was increased, that of 100 000 ppm chloride increased exponentially from approximately -25 mV. At 0 mV, the current density produced for tap water and 100 000 ppm chloride was -2.90E-05 and 4.54E-03 mA/cm^2 respectively. Highly saline solutions would clearly interfere with the determination of cyanide at an applied potential of 0 mV. According to Table 5.10 below, 100 000 ppm chloride began to react with silver between -100 and 0

mV. No interference from chloride was noticed at -100 mV, therefore setting the voltage set-point to -100 mV or less will eliminate interference from chloride ions.

Figure 5.7 **Cynoprobe voltammograms for chloride in water (1214 Ω, 35ºC, cylindrical silver electrode)**

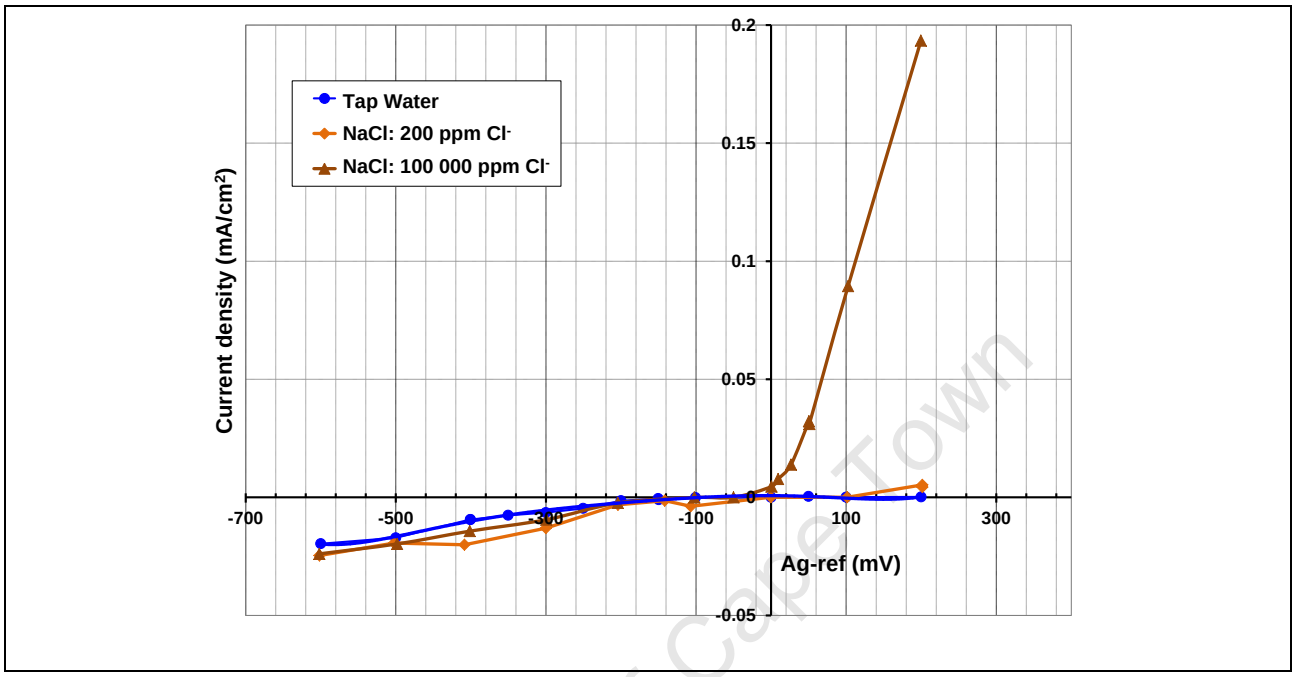


Table 5.10 **Applied potential and resulting current densities for 200 and 100 000 ppm chloride in deionised water, close to zero interference**

Set-point voltage (mV)	Resulting current density (mA/cm^2)		
	Tap water	200 ppm Cl$^-$	100 000 ppm Cl$^-$
-200	-2.40E-03	-3.16E-03	-2.39E-03
-100	-3.38E-04	-3.77E-03	-8.70E-05
0	-2.90E-05	2.23E-05	4.54E-03
10			7.73E-03
25			1.38E-02
100	5.28E-05	6.19E-05	8.94E-02
200	1.58E-04	5.28E-03	1.10E-01

5.4 CONCLUSION

The impact of metal cyanides and sulphur species, associated with the cyanidation of complex ores, on the Cynoprobe's free and WAD cyanide measurement was investigated.

Of the sulphur species that may form during the cyanidation of refractory sulphide gold ore, namely sulphide, thiocyanate, thiosulphate, sulphite, dithionate, tetrathionate, pyrosulphate and sulphate,

only sulphide and thiosulphate produced a positive interference during the analysis of blank and cyanide solutions at an applied potential of 0 mV. Sulphide may be present at the start of the leach of very sulphidic ores or in the residue where biological destruction of thiocyanate is employed, in concentrations <10 ppm. 10 ppm sulphide produced an analytical signal equivalent to approximately 20 ppm CN. In such cases, sulphide should be removed prior to the measurement of free cyanide by the addition of lead acetate or lead carbonate. For the measurement of WAD cyanide, lead sulphide should be filtered off before the addition of the LEX reagent, but the automatic, practical implementation of this will be difficult. Thiosulphate concentrations can vary between 200 and 600 ppm in real gold mining solutions. A concentration of 100 ppm thiosulphate in cyanide solutions produced a signal equivalent to 6-10 ppm CN. The plotting of voltammograms for blank and cyanide solutions containing thiosulphate showed that a voltage set-point of -150 mV will ensure that thiosulphate does not react with the silver electrode to produce a false signal.

Copper is the most common base metal associated with gold and it forms three copper cyanide species. The Cynoprobe's ability to recover WAD cyanide from all three copper cyanide species was determined by analysing solutions starved of and with excess free cyanide at pH 9.31 and pH 12. Recoveries were close to 100% for all solutions, except one, indicating that the Cynoprobe's ligand exchange technique with amperometric finish recovers WAD cyanide from the three copper-cyano species. After plant implementation, a coppery brown deposit was observed on the Cynoprobe's silver electrode that suppressed the reading and was suspected to be copper. The likelihood of copper plating out on the working silver electrode was therefore investigated by comparing copper and silver cyanide voltammograms. The copper cyanide reaction was initiated at approximately -750 mV. Therefore, at the Cynoprobe's typical set-point voltages copper would not plate out on the silver electrode. However, a stripping cleaning phase was introduced to the automatic cleaning cycle to remove deposits such as gypsum, where -1000 mV was applied to the electrode for a few seconds in the presence of 3% hydrochloric acid.

Western Australia, in particular is plagued by highly saline soil. Process mining water of many gold plants in Australia is therefore characterised by high salinity levels. Since there was a large market for Cynoprobe's in Australia, the effect of salinity on the cyanide measurement had to be investigated. Voltammograms for chloride indicated that a voltage set-point of -100 mV or less is required to eliminate positive interference from chloride ions.

Since plants treating sulphidic ore often include a flotation step in their circuit, reagents such as Xanthate, Betacol and Sasfroth 39 were also considered as potential interferents and were not found to interfere.

CHAPTER SIX

Joint implementation with cyanide destruction

6.0 CYANIDE DETOXIFICATION TECHNOLOGIES

As environmental awareness has increased, more gold mining companies have become signatories to the International Cyanide Management Code or been forced to comply with other regulatory bodies which require online free and WAD cyanide analysis with laboratory cross-checks. Especially in the cases where the required concentration limits are exceeded, a form of cyanide destruction is necessary to reduce the cyanide concentrations. During Cynoprobe trials on local plants, as discussed in Section 7.1.1, it was found that the residue WAD cyanide concentration was predominantly below the 50 ppm limit specified by the ICMI (International Cyanide Management Institute). Nevertheless, the general consensus amongst mining houses is to follow a more cautious policy and operate at tailings concentrations of say 50% of the limit. Some plants prefer to enforce the 0.5 ppm limit for effluents. As a result, there has been a great increase in the implementation of cyanide destruction for tailings and backfill materials worldwide.

There are several cyanide destruction processes that have proved successful in reducing the cyanide concentration of treated solutions and slurries to low levels at a number of mining sites worldwide. The SO_2/air INCO Process and Hydrogen Peroxide Process are the leading cyanide detoxification technologies. The SO_2/air INCO Process is the most widely implemented as it is applicable to both slurries and solutions and is relatively inexpensive to operate. The Hydrogen Peroxide having more expensive operating costs is often introduced as a finishing step to obtain low cyanide concentrations less than 1 ppm. Sodium metabisulphite and hydrogen peroxide are therefore often used together in a two-step addition method termed the Combinox Process. Caro's acid is the most efficient of the cyanide destruction technologies implemented by the gold mining industry. Alkaline chlorination was at one time the most widely applied cyanide destruction process but is now considered unsafe and is only used occasionally for small-scale operations.

In order for the Cynoprobe to be used to control and/or monitor the destruction of cyanide, it's compatibility with common chemical oxidants was investigated in the laboratory. These included sodium meta-bisulphite, hydrogen peroxide and peroxymonosulphuric acid. Chemical and process solutions to incompatibilities had to be found and implemented.

6.1 THE INCO SO_2/AIR-PROCESS

6.1.1 Blank tests

Blank solutions of sodium meta-bisulphite in tap water at pH 12 with and without LEX reagent were analysed in the Cynoprobe. No interference to the amperometric response was observed.

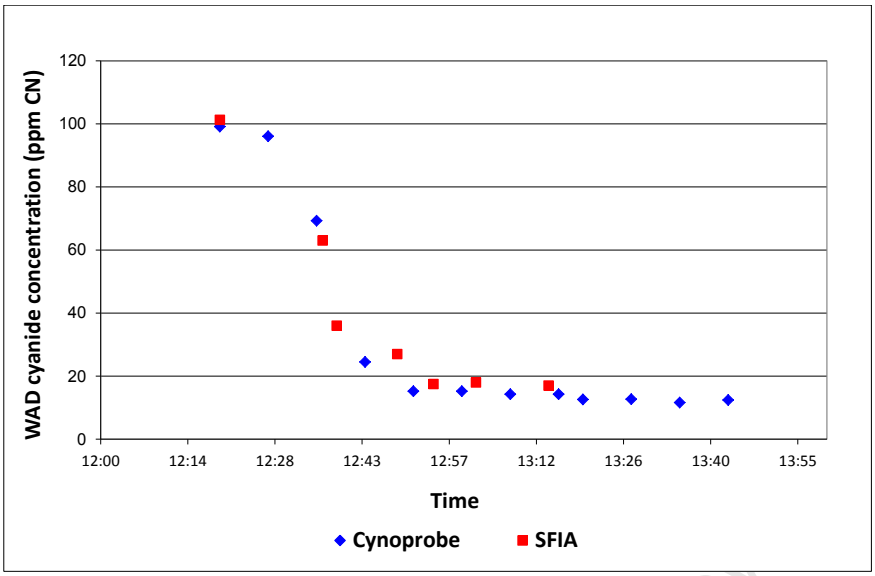
6.1.2 Destruction tests with Cynoprobe and SFIA

The Cynoprobe test instrument was calibrated with potentiostat board v1.0 (500 Ω resistance, 10-150 ppm CN, V_{sp} = -140 mV) and the glass amperometric cell with cylindrical electrode at 35ºC.

The Cynoprobe's compatibility with the SO_2/air process was tested in the laboratory with sodium meta-bisulphite as the oxidant in the presence of oxygen. The destruction of cyanide was monitored over an hour by the Cynoprobe and SFIA. Destruction occurred slowly, over an hour without the presence of a copper catalyst. The temperature of the solution remained at 23 °C. The initial pH of each solution was approximately 10.5 (at a pH of 12 no destruction occurs). As the reaction proceeded the pH dropped to about 6 due to the production of $NaHSO_4$.

Several free and WAD cyanide destruction tests were performed. Figure 6.1 shows the WAD cyanide destructions obtained from sodium meta-bisulphite in the presence of oxygen. Both the Cynoprobe and SFIA tracked the drop in WAD cyanide concentration from approximately 100 ppm to 15 ppm. The Cynoprobe tracked a further drop to 12.42 ppm so that 87.5% destruction was achieved. The samples analysed at similar times had an average absolute error of 3.14 ppm. This was equivalent to a percentage error of 11.1%. Hence, the Cynoprobe's WAD cyanide measurement appeared compatible with the INCO SO_2/air process and the LEX reagent; though a mild reductant was not destroyed by sodium meta-bisulphite.

Figure 6.1 **The destruction of WAD cyanide by sodium meta-bisulphite in the presence of oxygen, monitored by Cynoprobe and SFIA**



6.2 HYDROGEN PEROXIDE DETOXIFICATION

6.2.1 Blank tests

6.2.1.1 Hydrogen peroxide

Blank solutions of hydrogen peroxide in tap water at pH 12 with and without LEX reagent were analysed in the Cynoprobe. No amperometric response was produced in both cases, with a 'counts' value of zero. A fine cream/brown layer was observed on the working silver electrode which was most likely silver oxide. The deposit was cleaned off with steel wool so that the electrode was restored, but it was formed again when re-exposed to hydrogen peroxide. It was clear that hydrogen peroxide oxidises the silver electrode making it inert.

6.2.1.2 Cyanate

Blank solutions of 2000 ppm cyanate in tap water did not coat the silver electrode or produce any interference in the Cynoprobe.

6.2.1.3 Removal of negative interference from hydrogen peroxide

In an attempt to remove the negative interference and make the hydrogen peroxide process compatible with the Cynoprobe, a number of reducing agents were introduced in an attempt to

destroy peroxide in the Cynoprobe cell before measurement. A drop of 10% hydrazine, a very strong reducing agent effectively destroyed hydrogen peroxide, neutralising its effect on the silver electrode. It also did not affect the efficacy of the LEX reagent at all. However, because the neat form is an explosive poison, it is considered a hazardous substance and the availability of this reagent is limited. 2 mL of 4 M ascorbic acid, a mild reducing agent was added to the Cynoprobe cell, before measurement in the presence of hydrogen peroxide. After oxidation it took approximately ten readings for electrode to be restored. It also reacted with LEX reagent, making it incompatible. Sodium borohydride, a versatile reducing agent appeared to remove hydrogen peroxide interference, but also caused a further positive interference up to a cyanide equivalent of a few hundred parts per million. Finally, thiosulphate, a mild reducing agent was found to be effective in removing the negative interference from hydrogen peroxide. A concentration of ~5 ppm in the Cynoprobe cell removed the interference. It was also compatible with the LEX reagent.

Thiosulphates are relatively stable in high concentrations in neutral or alkaline solutions, but decompose to sulphite, sulphur and water in acidic solutions. Therefore, for hydrogen peroxide destruction applications, 0.5 mL of 1000 ppm thiosulphate solution (replaced every month) should be added to the Cynoprobe cell prior to measurement. This would obviously be a function of residual peroxide and should be tested for each application. A voltage set-point of -140 mV is also required, in order to ensure that thiosulphate causes no positive interference.

6.2.2 Destruction tests with Cynoprobe and SFIA

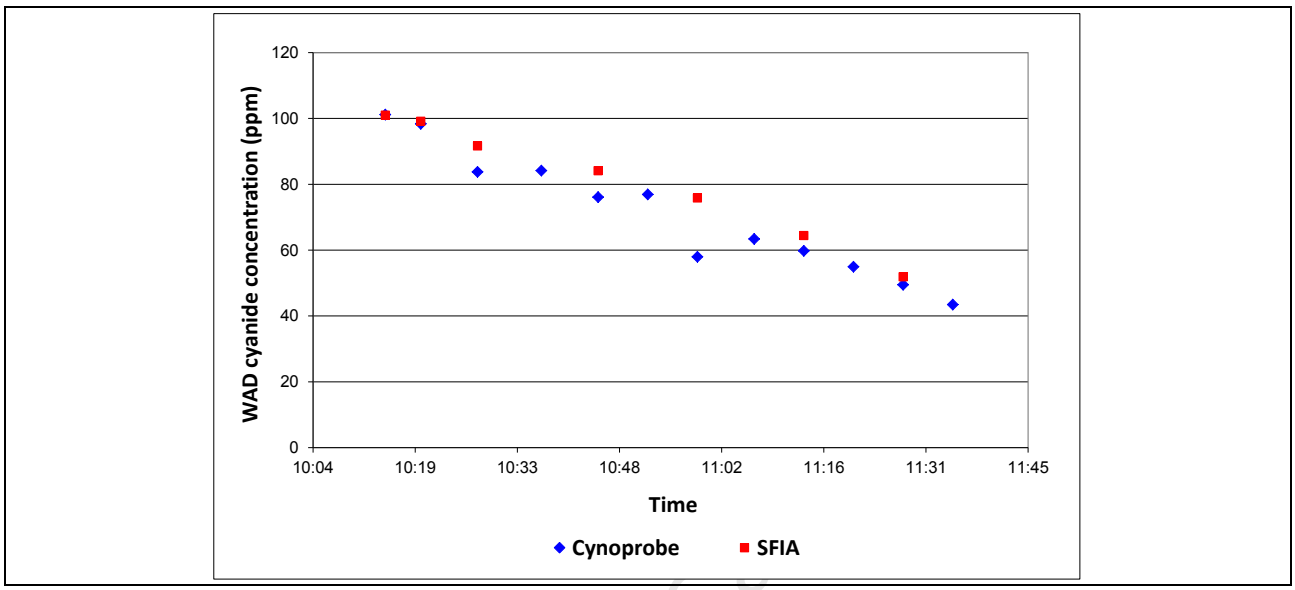
The Cynoprobe test instrument was calibrated with potentiostat board v2.0 (1214 Ω resistance, 10-100 ppm CN, V_{sp} = -140 mV) and the glass amperometric cell with cylindrical electrode at 35ºC.

The Cynoprobe's compatibility with hydrogen peroxide destruction, with removal of negative interference by sodium thiosulphate, was tested in the laboratory. A two-fold excess of hydrogen peroxide was added to 100 ppm free and WAD cyanide NaCN solution in the presence of a copper catalyst.

Figure 6.2 shows the destruction of 100 ppm WAD cyanide by hydrogen peroxide catalysed by copper and monitored by the Cynoprobe and SFIA. The initial pH of the solution was 9.3, which dropped to 8.1 by the end of the experiment. An initial redox potential of -21 mV became more positive and increased to 161 mV, indicative of an oxidising environment, by the end of the experiment. The temperature of the solution was 18.3 °C. According to the Cynoprobe, 101.17 ppm

WAD cyanide was reduced to 43.42 ppm, so that 57.1% destruction was achieved in approximately an hour and a half. The samples analysed at similar times had an average absolute error of 5.02 ppm. This was equivalent to a percentage error of 6.2%.

Figure 6.2 **The destruction of WAD cyanide by copper catalysed hydrogen peroxide, monitored by Cynoprobe and SFIA**



6.3 THE CARO'S ACID PROCESS

6.3.1 Blank tests

Blank solutions of Caro's acid in tap water at pH 12 with and without LEX reagent had the same effect as hydrogen peroxide, making the silver electrode inert. This was expected since Caro's acid is a mixture of peroxymonosulphuric acid, hydrogen peroxide and sulphuric acid. However, when a 1:1 molar equivalent was added to 100 ppm sodium cyanide solution the Cynoprobe responded with positive 'counts'. It appeared that the Caro's acid mixture reacted very specifically and quickly with cyanide so that there was not sufficient oxidant to react with the silver electrode.

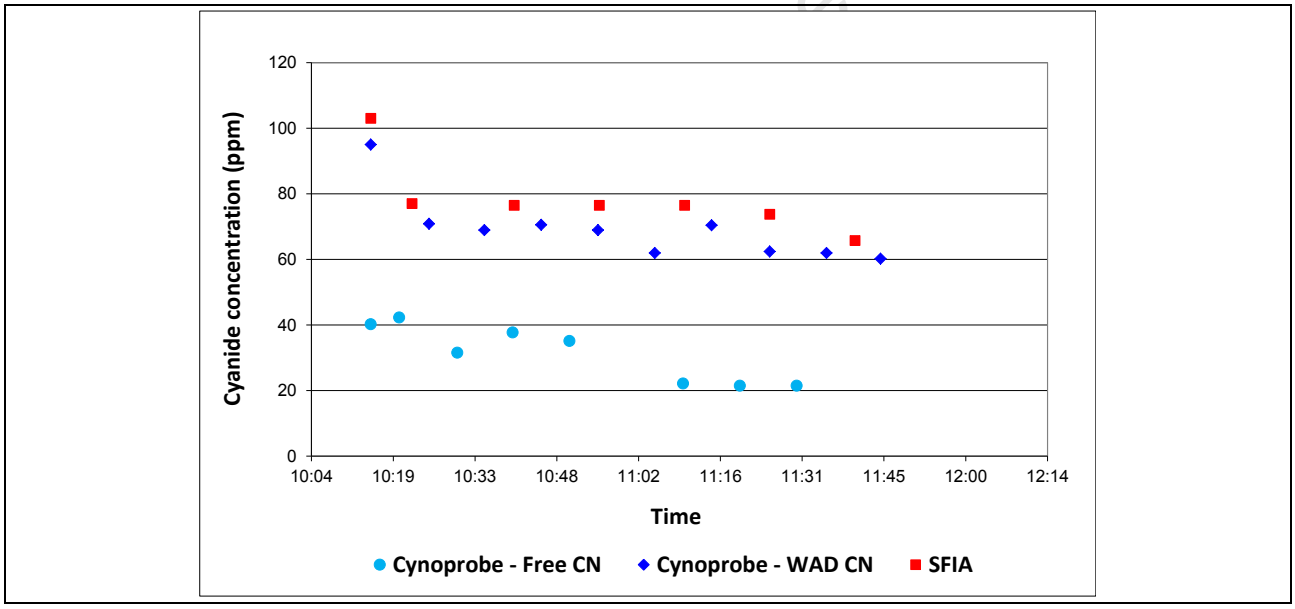
6.3.2 Destruction tests with Cynoprobe and SFIA

The Cynoprobe test instrument was calibrated with potentiostat board v2.0 (1214 Ω resistance, 10-100 ppm CN, V_{sp} = -140 mV) and the glass amperometric cell with cylindrical electrode at 35ºC.

To test for possible interferences in the Cynoprobe, Caro's acid was synthesised in the laboratory and a number of cyanide destructions were monitored by the Cynoprobe and compared to SFIA.

Freshly synthesised Caro's acid was added to 100 ppm free and WAD cyanide solutions in a 1:1 molar ratio and the destruction was monitored over an hour and a half. Upon Caro's acid addition the pH dropped to 3 but was immediately increased to 10 by adding sodium hydroxide. Figure 6.3 shows the partial destruction of 100 ppm WAD cyanide by Caro's acid as analysed by the Cynoprobe and SFIA. The initial WAD cyanide concentration of about 100 ppm dropped to ~70 ppm while the free cyanide concentration dropped to ~30 ppm after 15 minutes. A starch and potassium iodide dip stick indicated that no oxidant was present a mere five minutes after Caro's acid addition. The consumption of the oxidant and hence the destruction of cyanide with Caro's acid occurs almost immediately upon addition. After an hour and a half the free and WAD cyanide concentrations recorded by the Cynoprobe were 21.47 ppm and 60.20 ppm, respectively. 36.6% WAD cyanide destruction was achieved. The average absolute difference between the Cynoprobe and SFIA for samples taken at similar times was 6.07 ppm, with a percentage error of 7.7%.

Figure 6.3 The destruction of WAD cyanide by Caro's acid, monitored by Cynoprobe and SFIA



6.4 CONCLUSION

The compatibility of cyanide destruction oxidants in the Cynoprobe was investigated. SO_2/air and sodium meta-bisulphite did not show any interference. Interferences observed from hydrogen peroxide and Caro's acid were removed by adding a reducing agent (sodium thiosulphate) before measurement. The Cynoprobe's WAD cyanide measurement during sodium meta-bisulphite, hydrogen peroxide (with thiosulphate addition) and Caro's acid destruction was validated against SFIA. A percentage error of less than 10% was obtained in all cases, except for sodium meta-

bisulphite, which showed an error of 11.1% due to the low concentrations achieved. It is recommended that the Cynoprobe be calibrated at a high resistance and over a narrow concentration range when low concentrations are expected.

In the above experiments, the greatest degree of destruction was achieved with sodium meta-bisulphite, followed by hydrogen peroxide and lastly Caro's acid, with final WAD cyanide concentrations of 12.42 ppm, 43.42 ppm and 60.20 ppm which were equivalent to percentage destructions of 87.5%, 57.1% and 36.6%, respectively. Caro's acid is the most efficient oxidant of the three; however, it was only added as a molar equivalent, whereas both sodium meta-bisulphite and hydrogen peroxide were added in twofold excess. The lowest final concentration obtained during destruction with sodium meta-bisulphite was most likely due to volatisation of hydrogen cyanide at a pH of 6. The oxidants may be better compared by repeating the experiments at equivalent molarities and with pH control. However, the aim of the above experiments was not to evaluate the efficacy of the various destruction oxidants but rather to evaluate the Cynoprobe's WAD cyanide measurement, which was achieved.

CHAPTER SEVEN

Monitoring and control of cyanide addition and destruction

7.0 INDUSTRIAL IMPLEMENTATION

The development of an experimental prototype that measures WAD cyanide online involved the validation of the measurement technique in the laboratory. Pure and combination metal cyanide solutions mimicking plant filtrate were analysed to determine the statistical capabilities of the instrument (initial instrument precision and recovery). Possible interferences from complex ore types were tested and removed, and the compatibility of the instrument with common destruction oxidants was determined. The development of an industrial prototype involved an assessment of the robustness and accuracy of the measurement technique and instrument under plant conditions. Trials were firstly conducted on local gold plants so that intensive sampling campaigns could be run in conjunction with Mintek laboratories. Commercial implementation then led to exposure to complex ore types which required instrument refinements.

The Cynoprobe has been used to generate free and WAD cyanide trends suitable for monitoring regulatory compliance and for process control and optimisation. The frequency of the Cynoprobe's measurement cycle, approximately five minutes, makes it suitable for use in control schemes. Though beyond the scope of this thesis, it's free cyanide reading has been used to show the benefits of automatic cyanide addition control compared to manual control. Its WAD cyanide readings have been employed to optimise cyanide destruction. Proper cyanide addition and destruction control reduces cyanide consumption and results in less chemicals being discharged into the environment. Data trends from actual mines have been generated that show effective cyanide monitoring and control.

7.1 INDUSTRIAL CYNOPROBE MEASUREMENT VALIDATION

7.1.1 Witwatersrand basin gold plants (Westrand and Free State Goldfields)

A number of trials were conducted at local gold plants in the Westrand and Free State in order to validate the WAD cyanide measurement principle of the Cynoprobe for 'clean' ore types.

A typical installation in an enclosed, vibration free environment is shown in Figure 7.1. In this photo the Cynoprobe v2.0 Processor, Analyser and LEX units, the Air Purge unit, the pump and hydrogen peroxide and hydrochloric acid cleaning solution vessels were installed in a brick enclosure in the Carbon In Pulp (CIP) residue section near the residue sump at a gold plant on the Westrand.

Figure 7.1 A local Cynoprobe installation in the CIP residue section

1. Processor Unit, 2. Analyser Unit, 3. LEX Unit, 4. Air Purge Unit, 5. Pump, 6. Cleaning Solutions (3% hydrogen peroxide and hydrochloric acid)

Filtrate was sampled from a leach tank using a stainless steel filter probe and cage covered with a 10 micron sock. The sampling system also included an air purge unit to blow off slurry cake build up on the filter probe. Figure 7.2 shows the filter probe that was installed in a residue sump at a gold plant on the Westrand.

Figure 7.2 Stainless steel filter probe in residue sump

During a typical trial both the free and WAD cyanide measurements, together with pH and an alarm signal were logged to the plant PLC and Supervisory Control and Data Acquisition (SCADA) via the 4-20 mA signal output channels of the Cynoprobe. The plant metallurgist and/or operators were trained on the basic operation of the Cynoprobe and to take samples. Samples with a volume of 100 mL were taken by plant personnel, approximately every four hours for a few weeks; preserved with two drops 50% NaOH and stored in a cooler box until collected for analysis at Mintek. Sample times recorded by the plant operators were correlated with logged data, to compare the Cynoprobe and laboratory WAD cyanide measurements.

Inductively Coupled Plasma (ICP) multi-metal analysis performed on the filtrate samples revealed that copper (8-13 ppm) appeared to be the predominant source of weak metal-cyano complexes on local plants. Nickel and zinc were present in quantities of 0.4-2 ppm and 0.1-1 ppm (Table A.1, Appendix A). It should be noted that the ICP analysis results for each plant are not meant to be conclusive since they were only conducted on single spot samples, however collectively they give an idea of the WAD metal content of leach or residue filtrate from Witwatersrand ore. The LEX reagent dosage volume was therefore 2 mL 20% LEX reagent for all local trials.

7.1.1.1 Westrand gold plant - plant trial of first industrial prototype

The first industrial prototype of an online, free and WAD cyanide measurement device was installed on a local gold plant to measure the cyanide concentration of the seventh leach Pachuca. The instrument was calibrated with potentiostat board v1.0 (1000 Ω, 5-150 ppm, V_{sp} = -140 mV) and the glass amperometric cell with cylindrical electrode at 35ºC.

Figure 7.3 is a plot of the dataset logged over approximately two weeks during the trial. During this time, the free cyanide concentrations ranged between ~50 and 130 ppm, and the WAD cyanide concentrations ranged between ~60 and 150 ppm. This represents a large fluctuation in concentration which indicated the need for cyanide addition control. The free and WAD cyanide readings clearly followed a similar trend. The average difference between free and WAD cyanide over the two weeks was 25 ppm. Near the end of the data set the two trends show a convergence due to a slight change in the WAD metal content of the ore. Both the free and WAD cyanide concentration trends showed an increase in scatter at higher concentrations. Above 100 ppm the instrument was close to the maximum measurable concentration for the potentiostat board resistance of 1000 Ω.

Figure 7.3 **First industrial prototype trial at gold plant on the Westrand - free and WAD cyanide concentration of seventh leach pachuca**

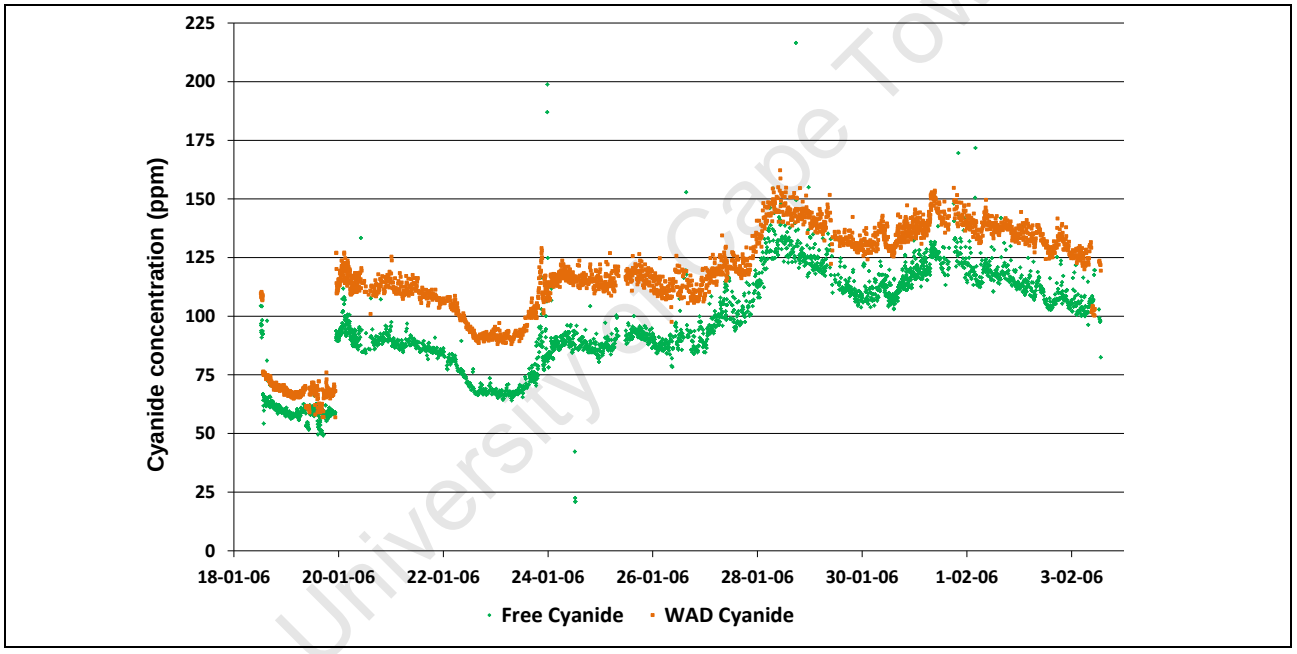
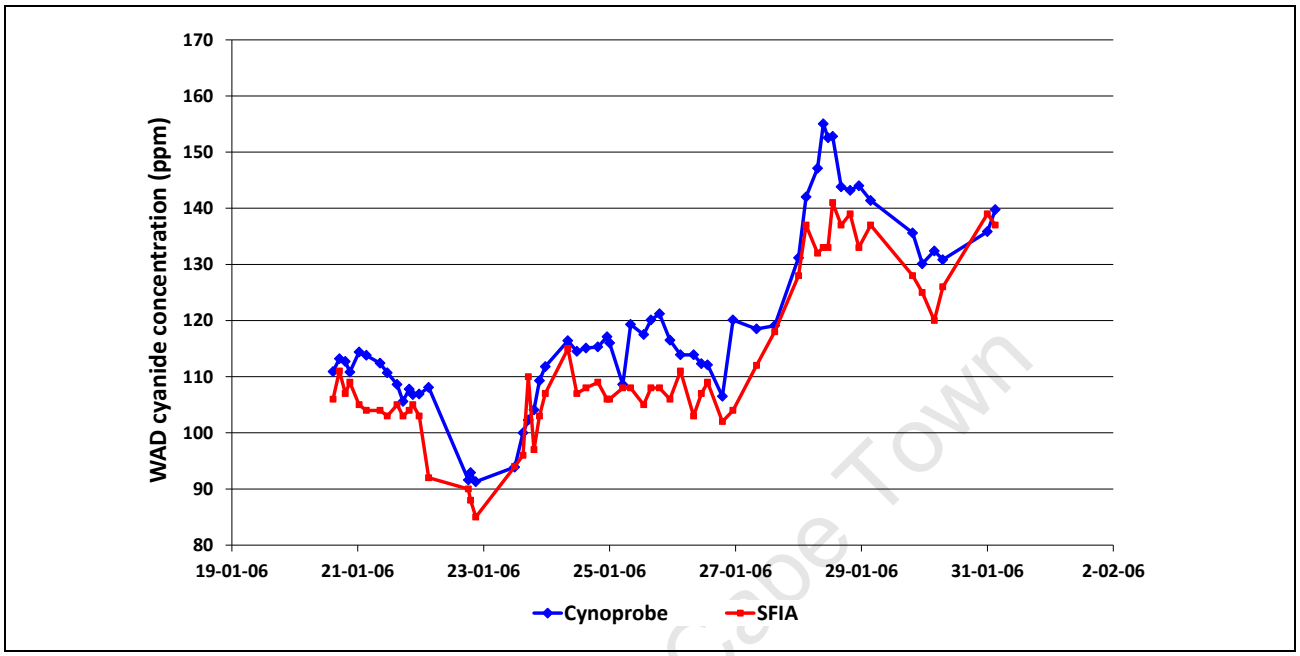


Figure 7.4 below is a comparison between the Cynoprobe and laboratory SFIA WAD cyanide results. It represents ten days' worth of data and sixty sample points. During this time, the WAD cyanide concentration varied significantly, from 91.3-155 ppm CN. The Cynoprobe and SFIA WAD cyanide analysis results followed similar trends. The Cynoprobe therefore accurately picked up the changes in the WAD cyanide concentration that SFIA did. The Cynoprobe's sensitivity to and ability to respond quickly to changes in the WAD cyanide concentration is evident.

The average absolute difference between SFIA and Cynoprobe was 7.25 ppm. This represents an average percentage error of **6.4%**. This difference may be explained primarily by the decay of cyanide. Though samples were preserved with NaOH and stored in a cooler box with ice that was

replenished twice a week, it was not possible to maintain low temperatures, being the middle of summer.

Figure 7.4 **First industrial prototype trial at gold plant on the Westrand - validation of Cynoprobe WAD cyanide reading compared to Mintek laboratory SFIA**



7.1.1.2 Other Witwatersrand gold plant trials

After a successful plant trial with the first industrial prototype in January 2006, other local plants expressed interest in site trials to validate the Cynoprobe's WAD cyanide analysis technique.

Three other trials were conducted at gold plants on the Westrand and Free State to compare the Cynoprobe's WAD cyanide reading with laboratory results. Three weeks data from a CIP residue tank where the WAD cyanide concentration ranged between 5 and 50 ppm produced an average percent error of **9.9%** compared to SFIA, performed at Mintek's laboratories. Eight days data from two backfill tanks with cyanide destruction by ferrous sulphate addition, where the WAD cyanide concentration ranged between 7 and 30 ppm showed an average percent error of **9.6%** compared to SFIA. Finally, 4 days data from the last tank of a CIL circuit where the WAD cyanide concentration ranged between 40 and 70 ppm, showed an average percentage error of **7.3%** compared to results from the OI Analytical FS 3100 instrument.

7.1.2 International gold plants

After successful trials at local plants, installations were rolled out on an international scale. Data has been obtained illustrating the validity of the Cynoprobe's WAD cyanide readings for complex ore types.

7.1.2.1 High copper

7.1.2.1.1 WAD cyanide reading - Australian gold plant

A number of Cynoprobe v3.0 instruments were installed at a gold and copper plant in Australia, to achieve overall cyanide management (cyanide addition and destruction control and environmental monitoring). The plant processes ore from an Archaean Greenstone Belt. Three leach filtrate samples were brought back to Mintek for cyanide, metal and chloride analysis. The results are shown in Table 7.1 below and in Table A.2 (Appendix A). The WAD bound cyanide was equivalent to ~85 ppm, which was due to copper concentrations of ~40 ppm, according to Inductively Coupled Plasma (ICP) multi-metal analysis. Nickel and zinc were present in quantities of 0.5 ppm and ~6 ppm. The difference between Total and WAD cyanide accounted for ~10 ppm cyanide bound to iron, agreeing with low iron concentrations of <0.2 ppm according to ICP analysis. Both the iron and sulphur content of the ore was low, with low SCN concentrations in the leach of ~45 ppm (S[CN] = ~20 ppm). Brine in the process water was low at this plant, with ~0.4 ppm chloride.

Table 7.1 Australian gold plant No.1 – spot sample analyses

Sample	Titration (ppm)	SFIA WAD CN (ppm)	SFIA Total CN (ppm)	SFIA TOT+ S[CN] (ppm)	Conductivity (mS.cm-1)	pH	Redox potential (mV)	Chloride (g/L)
Leach filtrate 1	115.9	175.0	199.0	223	1.40	9.68	27	0.89
Leach filtrate 2	116.6	217.0	221.0	245	1.69	9.78	55	0.20
Leach filtrate 3	114.2	198.0	212.0	224	1.69	9.78	55	0.20
Average	115.6	196.7	210.7	231	1.59	9.75	46	0.44

Figure 7.5 shows the Cynoprobe v3.0 instrument installed in the CIL and destruction sections of the plant, monitoring the WAD cyanide concentration of the CIL tails pre and post destruction and recirculated water pre and post further destruction. The instrument was calibrated with potentiostat board v2.0 (354.2 Ω, 20-300 ppm CN, V_{sp} = -140 mV) and the glass amperometric cell with

cylindrical electrode at 25ºC. The LEX reagent dosage volume was set to 2 mL 20% LEX reagent per WAD cyanide measurement.

Figure 7.5 Cynoprobe v3.0 installation at Australian gold plant

1. Processor Unit, 2. Analyser Unit, 3. LEX Reagent, 4. Air Purge Unit, 5. Pump, 6. Cleaning Solutions (2% hydrogen peroxide and hydrochloric acid)

At the end of 2009 and beginning of 2010, a comparative study between the online Cynoprobe measurement and laboratory WAD cyanide assays was performed on the CIL tails. Samples were analysed using the FS 3100 instrument and the distillation method at onsite and local commercial laboratories respectively. Table 7.2 below shows the results obtained. During the five months the WAD cyanide concentration fluctuated between 55 and165 ppm. A total of eleven complete data sets were available for statistical comparison.

Table 7.2 Australian gold plant No.1 trial – WAD cyanide measurement of CIL Tails by Cynoprobe, FS 3100 and distillation

Date and Time	Cynoprobe (ppm)	FS 3100	Laboratory distillation
2009-10-04 07:30	117.0	126.0	-
2009-10-06 09:10	147.0	129.0	-
2009-10-11 10:45	170.6	170.7	-
2009-10-29 12:30	115.6	123.43	140
2009-11-05 07:00	128.0	91.0	140
2009-11-10 07:30	140.5	133.0	-
2009-11-12 08:50	150.7	147.9	140
2009-11-01 09:15	86.3	83.35	120
2009-11-23 08:30	160.4	-	-
2009-11-26 08:20	134.3	142.6	110
2009-11-30 09:40	157.5	-	-
2009-12-03 08:00	165.1	142.7	120
2009-12-07 13:00	62.0	58.0	55
2009-12-10 09:40	157.5	152.7	110
2009-12-21 12:10	149.0	145.7	150
2009-12-24 07:45	168.2	167.9	-
2009-12-28 07:12	156.8	151.2	-
2009-12-31 09:00	98.0	98.5	-
2010-01-07 09:30	121.7	115.2	130
2010-01-15 09:00	167.3	155.8	NA
2010-01-18 00:00	136.4	133.1	150
2010-01-21 07:10	131.3	127.4	150
2010-01-25 07:10	102.2	98.8	-
2010-01-28 10:00	119.5	113.0	-
2010-02-04 10:30	101.8	83.2	-
2010-02-08 06:15	97.2	98.0	-
2010-02-22 08:15	125.4	115.8	-

Table 7.3 shows the statistical parameters obtained for the eleven retained values. Over the five months, the pooled mean WAD cyanide concentration in the final leach tank was 124.1 ppm WAD CN.

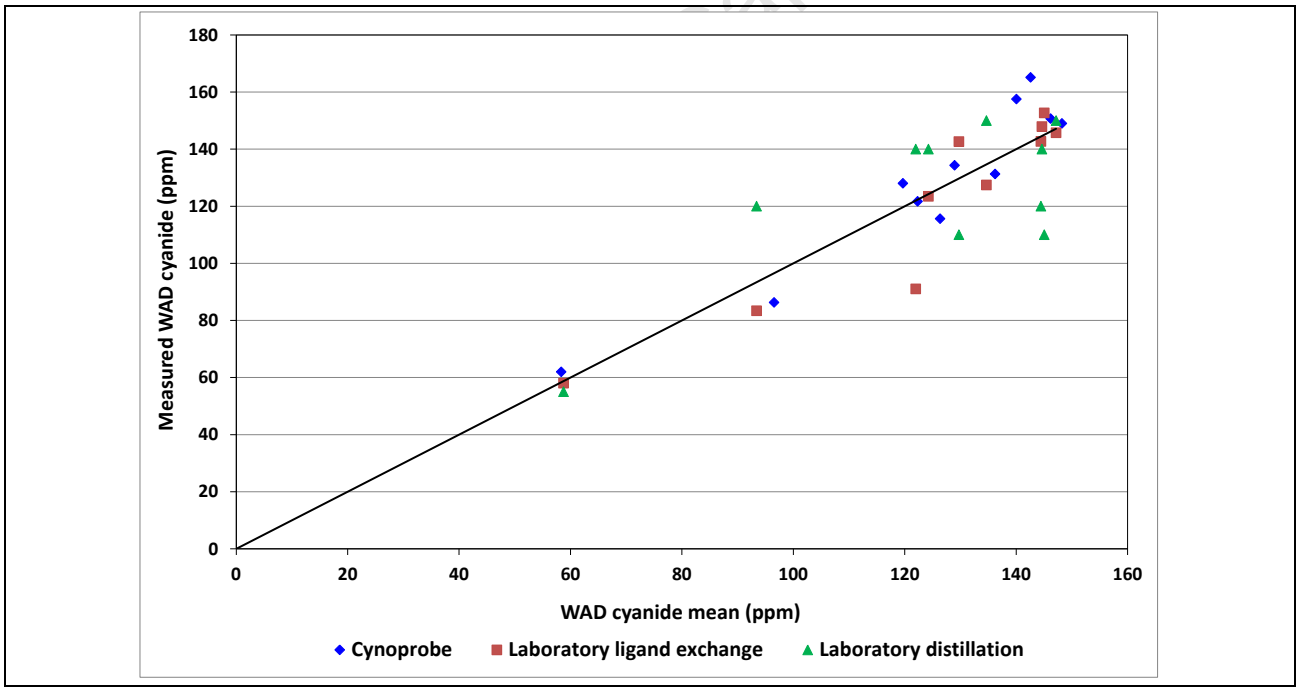
Figure 7.6 below is a scatter plot comparing the actual measured WAD cyanide measurements of each method with the mean of all methods. Though the mean laboratory distillation concentration showed no difference from the pooled mean, its actual measured values deviated most from the average concentration of each sample, with an R^2 value of 0.547. The Cynoprobe results correlated best with the mean with an R^2 value of 0.897. This was followed closely by the FS 3100 instrument with an R^2 value of 0.873. The bias of all the methods was acceptable at <5%. The leaching

residence time was five days. The standard deviation of each five day set was therefore calculated using the complete dataset shown in Table 7.2. The Cynoprobe was the most precise with a percentage RSD of 7.1%, followed by the FS laboratory ligand exchange method at 9.7%. Results from the laboratory distillation were imprecise at 16.1%.

Table 7.3 **Australian gold plant No.1 trial – statistical comparison of Cynoprobe, FS 3100 and laboratory distillation WAD cyanide measurements**

Statistic	Pooled Mean	Cynoprobe	FS 3100	Laboratory distillation
Retained values	11	11	11	11
Mean (ppm)	124.1	127.4	120.9	124.1
Correlation, R^2		0.897	0.873	0.547
Difference (ppm)		3.3	-3.2	0.0
Bias, percent		2.6%	-2.6%	0.0%
Standard Deviation		9	12	20
Percent RSD		7.1%	9.7%	16.1%

Figure 7.6 **Australian gold plant No.1 trial – actual versus mean WAD cyanide concentrations for Cynoprobe, FS 3100 and laboratory distillation**



According to the statistical comparison of the three methods the laboratory distillation results suffered from excessively high variability compared to the pooled mean. Therefore, the FS 3100 results were used to validate the online WAD cyanide measurements of the Cynoprobe at this plant. Comparative data for the Cynoprobe and FS 3100 instruments was available for twenty five samples. The average, absolute difference between the Cynoprobe and FS 3100 was calculated

and found to be minimal at 7.94 ppm. This was equivalent to an average percentage error of **6.2%**.

For a copper concentration of 40 ppm and total WAD cyanide concentration of 125 ppm, the copper to cyanide molar ratio is 1:8. According to the Mintek speciation spread-sheet, at pH 9.75 and redox potential 46 mV, $[Cu(CN)_3]^{2-}$ is the predominant copper cyanide species in solution with a concentration of ~47 ppm. $[Cu(CN)_4]^{3-}$ and $[Cu(CN)_2]^{-}$ are present in insignificant concentrations of ~2 ppm and 0.1 ppm respectively. The theoretical concentration of the cyanide and hydrogen cyanide ions was ~59 ppm and ~17 ppm, respectively. The correlation between the Cynoprobe and laboratory FS 3100 with percent difference of 6.2% validates the Cynoprobe's WAD cyanide analysis technique in the presence of copper. The Cynoprobe's ligand exchange technique with amperometric finish recovers WAD cyanide from the most common copper cyanide species, $[Cu(CN)_3]^{2-}$.

7.1.2.2 High sulphur – North American gold and copper mine

The Cynoprobe v2.0 instrument was installed at a gold and copper mine in North America. It was set up to measure the online WAD cyanide concentration of the first and fifth leach tanks. The LEX reagent dosage volume was set to 4 mL 20% LEX reagent per WAD cyanide measurement. Initially interference from thiosulphate resulted in 100% over-recovery of WAD cyanide by the Cynoprobe, compared to the OIA-1677 standard test method. The plant processes Carlin-type ore that is characteristically refractory with gold locked in pyrite and arsenopyrite. The cyanidation leach slurry is consequently rich in copper and sulphur species, with copper, thiosulphate and thiocyanate concentrations up to 80 ppm, 4000 ppm and 2000 ppm respectively. Subsequent to a laboratory investigation to remove thiosulphate interference the voltage set-point on the Cynoprobe's potentiostat board was adjusted. Thiosulphate interference is attenuated by applying a lower working potential of -150 mV versus the Ag/AgCl reference electrode (see Section 5.1.3.3). Slurry filtrate samples were taken from the first, second and fifth leach tanks in order to validate the Cynoprobe's WAD cyanide measurement against the OIA-1677 standard test method. Samples were analysed in quadruplicate by both methods. The results obtained, based on averages, are summarised in Table 7.4 and show the removal of thiosulphate interference to the Cynoprobe's WAD cyanide reading. There was an excellent agreement between the analytical data obtained with the Cynoprobe and the reference method. A percentage error of less than 10% was obtained for all samples. The percent relative standard deviations based on the average readings of the Cynoprobe and Method OIA-1677 were <2% and <5%, respectively. The average, absolute difference between the two methods was 4.10 ppm. An average percentage difference of **4.5%**, with respect to the laboratory method was therefore obtained.

Table 7.4 WAD cyanide analysis of CIP filtrate containing thiosulphate - comparison between Cynoprobe (V_{sp} = -150 mV) and laboratory method OIA-1677 analyses

Date	Sampling Point	WAD cyanide by Cynoprobe (ppm)	WAD cyanide by OIA-1677 (ppm)	Δ WAD (Cynoprobe - OIA) (ppm)	Percent error
2007-09	CIP Tank 1	116.1	120.7	4.6	3.8%
2007-09		113.6	115.6	2.0	1.8%
2007-09		116.7	114.1	-2.6	2.3%
2010-11	CIP Tank 2	34.2	35.8	1.6	4.5%
2010-11		31.3	33.8	2.5	7.5%
2007-09	CIP Tank 5	125.6	119.2	-6.4	5.4%
2007-09		121.2	122.8	1.6	1.3%
2007-09		131.0	119.7	-11.3	9.4%

7.2 CYANIDE DESTRUCTION CONTROL

The Cynoprobe may be used to monitor and/or control the destruction of cyanide. As shown in Chapter 6, the Cynoprobe's compatibility with the most common destruction oxidants was tested in the laboratory; namely, sodium metabisulphite, hydrogen peroxide and peroxymonosulphuric acid.

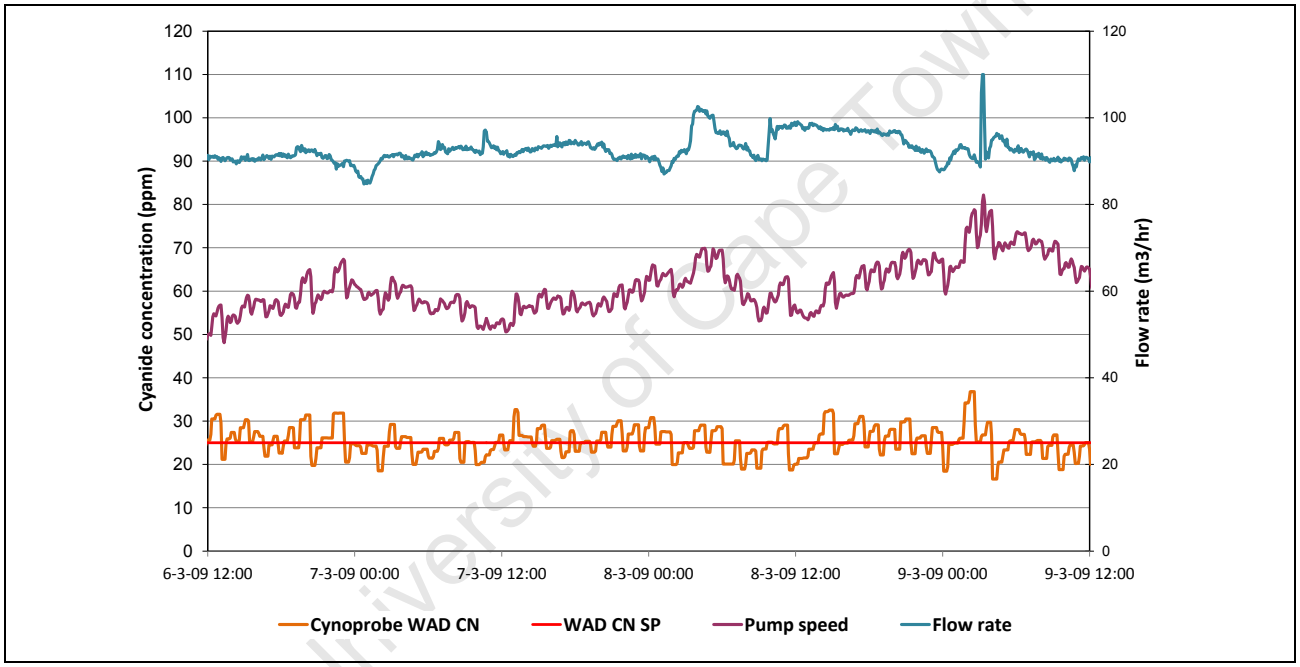
7.2.1.1 Caro's Acid Destruction

In 2008, a Cynoprobe v2.0 instrument was installed in the Caro's acid destruction circuit of a gold mine in Australia. The instrument was calibrated with potentiostat board v1.0 (1000 Ω resistance, 5-100 ppm CN) and the glass amperometric cell with cylindrical electrode, at 35ºC. The LEX reagent dosage volume was set to 2 mL 20% LEX reagent.

Caro's acid is produced in situ in an adiabatic process. 70% hydrogen peroxide (H_2O_2) and 98% sulphuric acid (H_2SO_4) are mixed in a short residence time mixer reactor to form Caro's Acid (H_2SO_5). Being a very exothermic reaction, the temperature of the Caro's acid reactor typically rises rapidly to about 95ºC. The hot Caro's Acid leaving the reactor is then quenched by the addition of water so that the temperature remains less than 45ºC. The quenched Caro's acid is then discharged directly into a small stirred tank where contact is made with the process tailings slurry. The pH of the leach slurry decreases as the Caro's acid is added. A pH probe in the detox tank is linked to lime supply so that the pH in the tank is maintained at a minimum of 9. This ensures the efficient and safe destruction of the cyanide.

The filter probe was installed in the detox tank to obtain filtrate for the determination of the final cyanide concentration levels in the Cynoprobe. The online WAD cyanide concentration reading was then linked to a cyanide destruction control algorithm in order to control Caro's acid addition and ensure that the discharge WAD cyanide concentration was approximately 50% of the prescribed ICMI limit of 50 ppm. Inputs to the controller included flow rate, pump speed and WAD cyanide concentration. The Cynoprobe WAD cyanide cycle time was approximately 10 minutes. Data taken over three days is shown in Figure 7.7. The WAD cyanide concentration fluctuated between 17 and 37 ppm. Overall, relatively tight control of the WAD cyanide concentration to the set-point of 25 ppm was achieved.

Figure 7.7 **Caro's acid destruction control utilising the Cynoprobe's online WAD cyanide concentration reading**



7.3 ENVIRONMENTAL MONITORING

Online analysis may be used to monitor the WAD cyanide concentration of leach or destruction effluent, for environmental purposes. Auditors from ICMI and national or local authorities require that online analysis be used to monitor the WAD cyanide concentration so that the upper uncertainty range of the data is sufficiently clear of the criteria limits. For example, for ICMI regulatory compliance to the effluent limit of 50 ppm WAD CN, generated online data should be say 50% of the permissible levels, 99% would not be acceptable, statistically non-compliant with a high probability. The closer to the criteria levels, the more validation and cross-checking via standard laboratory methods should be done (quote: Peter Lotz (ICMI Technical Expert Auditor), 2012). Accredited laboratories utilising standard methods should be used to validate any in-house or online analysis.

Online measurements also give the plant management and auditors a more accurate idea of the weighted average than grab sample analyses. For example, a cyanide spike detected by a grab sample will grossly affect the average and may lead to the false notion that the weighted average is beyond limits. The many consistent readings of online analysis will 'average out' the spike, giving a better idea of the general trend.

7.3.1 Cynoprobe application to environmental discharge

In 2006, the Cynoprobe v2.0 instrument was installed at a mine in West Africa that processes very refractory ore consisting mostly of arsenopyrite with some quartz free gold. As a result, the ore is cyanide consuming and produces slurry rich in arsenic and oxidised sulphur species such as thiocyanate. Since process water is discharged into natural waterways during the rainy season and some of the ponds are utilised by the local community, the mine has a water treatment plant in order to remove arsenic and cyanide. Arsenic and heavy metals are removed by a system of flocculation and settling after addition of ferrous sulphate and potassium permanganate. Detox feed samples brought back to Mintek for arsenic analysis had concentrations up to 11 ppm with an average concentration of 4 ppm for seven samples (Table A.2**Error! Reference source not found.**, Appendix A). WAD cyanide concentrations are reduced to below the limit of 0.6 ppm as specified by the Environmental Protection Agency (EPA). After natural degradation in the tailings dam the water is treated by biological destruction. The Detox feed has typical WAD cyanide concentrations of 3-8 ppm and thiocyanate concentrations of up to 500 ppm. *Pseudomonas* bacteria oxidise cyanide and break down the thiocyanate compound to release sulphur. It is therefore essential to run the plant with sufficient oxygen. Table A.2 in Appendix A shows typical sulphate levels before and after destruction, <0.02 and >1000 ppm respectively.

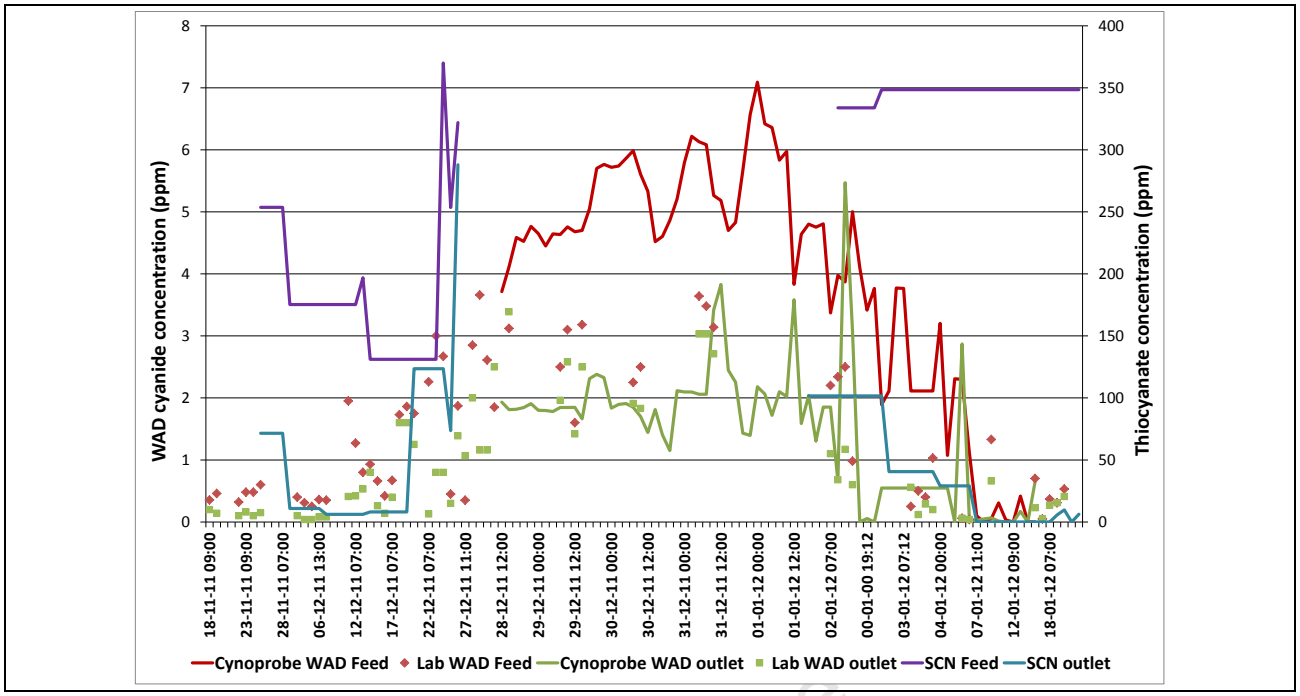
The Cynoprobe was set up to measure the WAD cyanide concentrations online before and after destruction. In 2009, it was retrofitted and calibrated for low concentrations with potentiostat board v2.0 (4020 Ω, 0.3-30 ppm CN) with the polystone/PVC amperometric cell with cylindrical electrode, at 35ºC. The LEX reagent dosage volume was set to 2 mL 20% LEX reagent. 0.5 mL of 1000 ppm thiosulphate was also added prior to measurement in order to remove residual permanganate which oxidised the silver electrode, making it inert. The online measurements are frequently checked in the laboratory onsite. Samples are taken from the destruction ponds every shift and analysed in the laboratory for WAD cyanide as well as thiocyanate. WAD cyanide analysis is performed by the picric acid method and thiocyanate by Ion Chromatography (IC).

In January 2012, the author was commissioned to conduct a laboratory consultation on the cyanide analysis methods used to monitor the cyanide concentration of the discharge that a local community has access to. Figure 7.8 below is a graphical representation of the recorded online and laboratory data from 18 November 2011 to 18 January 2012. Before 8 December, WAD cyanide concentrations of the Detox feed and outlet were low, <0.60 ppm and <0.20 ppm respectively, according to the picric acid method. By 28 December, these had increased to 3.66 ppm and 3.39 ppm respectively, according to the picric acid method. No data was available for the Cynoprobe before 28 December due to PLC failure. However, according to the Cynoprobe, the WAD cyanide concentrations continued to increase and fluctuated between 4.52 and 7.09 ppm for the feed and 1.15 and 3.80 ppm for the outlet, from 29 December 2011 until 1 January 2012. During this time, the WAD cyanide concentration was above the upper detection limit of the picric acid method, and the results were therefore incorrect. This clearly shows the versatility of the online amperometric method that is able to measure a wider concentration range than the picric acid method. According to IC, the thiocyanate concentrations of the feed were normal before 27 December, ranging from 131.1 to 370.0 ppm. However, the outlet concentrations increased from 8.1 to 123.6 ppm by 19 December and still further to 288.0 ppm by 27 December.

The outcome of the investigation showed that the accumulation of WAD cyanide or thiocyanate in the treatment pond could be environmentally harmful. A thiocyanate limit of 10 ppm is considered to be protective of aquatic life, provided the pond is sufficiently aerated. The EPA WAD cyanide limit of 0.6 ppm was exceeded on 14 December with a recorded value of 0.80 ppm.

This investigation illustrates the need to monitor both WAD cyanide and thiocyanate in order to avoid aquatic life fatalities, even though thiocyanate measurement is not a regulatory requirement. The data also showed that the Cynoprobe was more effective than the picric acid method in monitoring the WAD cyanide concentration over this period. It illustrates the pitfalls of the picric acid method that relies on dilution.

Figure 7.8 **Environmental monitoring - online and laboratory WAD cyanide and thiocyanate measurements**



7.4 CONCLUSION

7.4.1 Wide scale validation

The Cynoprobe's WAD cyanide measurement was validated during industrial trials at local and international gold plants processing both simple and complex ores.

Data associated with 'clean' Wits type ore, and copper and sulphur rich ore was presented in Section 7.1. The Cynoprobe's WAD cyanide reading was successfully validated in the presence of high copper concentrations such as 40 ppm and 80 ppm copper with copper to cyanide molar ratios of 1:8 and 1:3.5 respectively and $[Cu(CN)_3]^{2-}$ being the predominant species. It was also validated in the presence of <14 ppm copper and excess free cyanide with significant proportions of $[Cu(CN)_4]^{3-}$ expected. Therefore, it may be concluded that the ligand exchange reagent recovers WAD cyanide from the various cuprous cyano complexes, as explained in Section 5.2.1. The removal of thiosulphate interference by adjusting the applied potential, as discussed in Section 5.1.3.3, proved effective at a copper/gold mine in North America with thiosulphate and thiocyanate concentrations of 700-4000 ppm and 2000 ppm, respectively.

Sufficient data was therefore collected to establish that the Cynoprobe is reliable and its measurements are accurate and reproducible for concentrations ranging from 5-155 ppm. The

Cynoprobe's WAD cyanide reading produced an accuracy of greater than 90% with respect to laboratory methods; SFIA and FS laboratory ligand exchange.

7.4.2 Cyanide Process Control

The online WAD cyanide concentration reading of the Cynoprobe was linked to a cyanide destruction control algorithm in order to control Caro's acid addition and ensure that the discharge WAD cyanide concentration was approximately 50% of the prescribed ICMI limit of 50 ppm. Data was obtained over three days which showed relatively tight cyanide control to within approximately 10% of the set-point of 25 ppm WAD CN.

7.4.3 Environmental monitoring

Online analysis may be used to monitor the WAD cyanide concentration of leach or destruction effluent, for environmental regulatory purposes. For approximately six years, the Cynoprobe has been monitoring the free and WAD cyanide concentrations before and after biological destruction at a gold plant under environmental scrutiny that processes arsenopyrite. Process water is discharged into natural waterways during the rainy season and some of the ponds are utilised by the local community. The EPA requires that the WAD cyanide concentration levels of the discharge be maintained to below 0.6 ppm. The Cynoprobe's online measurements are frequently crosschecked with laboratory WAD cyanide analysis using the picric acid method. Thiocyanate is also determined by IC. In January, 2012, the recent cyanide and thiocyanate concentration levels of the discharge to the tailings dam were examined and the online and laboratory measurements compared. High WAD cyanide and thiocyanate levels, due to mismanagement of the water balance, were found to be potentially toxic. Though the measurement of thiocyanate is not a regulatory requirement, plants should regularly analyse thiocyanate concentrations in order to avoid aquatic life fatalities. A limitation of the picric acid method, which relies on correct dilution, was also shown. WAD cyanide concentrations greater than 4 ppm, as analysed online by the Cynoprobe, were not detected by the picric acid method.

CHAPTER EIGHT

Conclusion and future work

An online free and WAD cyanide analyser was developed to facilitate the measurement and control of cyanide on gold plants. The free and WAD cyanide measurements were based on amperometry and ligand exchange, respectively. An organic ligand exchange reagent was employed to displace the cyanide ion from copper, nickel, zinc and silver, before measurement by amperometry. Average overall WAD cyanide recoveries from pure metal cyanide standards with concentrations ranging from 0.5-100 ppm indicated that the reagent was most effective for copper (90-96%) and zinc (89-97%), followed by nickel (73-91%). Higher recoveries from nickel, close to 100% were obtained by increasing the concentration of LEX reagent. Initial and on-going recovery and precision for metal cyanide standards (pure and combination metal cyanide solutions) were 89-97% (<8.5% RSD) and 81-100% (<4.5% RSD). These statistics are comparable to the standard test methods; ASTM D-6888-04 which demonstrates an initial recovery and precision of 70-114% (<11.1% RSD) and Method OI-1677 which demonstrates an on-going recovery and precision of 82-132% (<11% RSD).

The instruments detection limit (DL), lower quantification limit (LQL) and upper quantification limit (UQL) were determined based on a desired confidence level of 95%, for the various resistances of the two potentiostat boards currently used in the Cynoprobe. For potentiostat board v1.0 a DL and LQL of 0.10 ppm and 0.30 ppm was obtained indicating the lowest concentrations that may be measured. For potentiostat board v2.0, a DL and LQL of 0.04 ppm and 0.10 ppm, respectively, was obtained. The maximum concentrations that were measured (UQL) with potentiostat board v1.0 and 2.0 were 2500 ppm and 3800 ppm, respectively. The measurable concentration ranges for each resistance are shown in Table 4.16. Across the entire range of resistances for both boards, a percent relative deviation ≤7.2% was obtained.

For optimal recovery of WAD cyanide from typical gold plant filtrate, the following parameters were required:

- volume of ligand exchange reagent - 2 mL and 4 mL 20% LEX reagent for normal (<80 ppm) and high (300 ppm) base metal (copper, zinc, silver) concentrations respectively, 6 mL 10% reagent may be required for significant nickel concentrations (<60 ppm).
- amperometric applied potential - -140 mV to ensure that the LEX reagent did not react with the working silver electrode to produce a false analytical signal.

- LEX reagent reaction time - approximately 5 minutes.
- Set-point temperature - 35ºC (insensitivity of recovery to temperature from 20-30ºC and 40-45ºC allows for adjustment according to location temperature and season).

The instruments applicability to complex ore types was investigated by determining the impact of sulphur species and metal cyanides on its free and WAD cyanide reading. Of all the sulphur species that may form during the cyanidation of refractory sulphide gold ore, only sulphide and thiosulphate produced interferences. Laboratory experiments showed that sulphide interference may be removed by the precipitation of lead sulphide prior to measurement with the addition of lead acetate or carbonate. A voltage set-point of -150 mV prevented thiosulphate from reacting with the silver electrode to produce a false signal. The WAD cyanide recoveries of copper cyanide solutions starved of and with excess free cyanide were also determined and found to be close to 100% at pH 9.31. The probability of copper plating out on the working silver electrode was found to be low. The copper and silver cyanide voltammograms showed that copper reacts with cyanide at a lower potential than silver.

In order for the Cynoprobe to monitor and control cyanide destruction, its WAD cyanide reading in the presence of common oxidants had to be validated in the laboratory. Sodium meta-bisulphite did not show any interference. Interferences observed from hydrogen peroxide were removed by adding a reducing agent (sodium thiosulphate) before measurement. The Cynoprobe's WAD cyanide measurement during sodium meta-bisulphite, hydrogen peroxide (with thiosulphate addition) and peroxymonosulphuric acid destruction was validated against SFIA, so that percentage errors close to 10% were obtained in all cases.

Since 2006, the Cynoprobe has been implemented commercially on gold plants worldwide. The Cynoprobe's WAD cyanide measurement has therefore been validated at local and international gold plants processing both simple and complex ores. WAD cyanide was recovered from copper cyanide species in process solutions containing both high and low copper concentrations; 80 ppm and <14 ppm, respectively. The effective removal of thiosulphate interference by adjusting the applied potential to approximately -150 mV was shown at a copper/gold mine with thiosulphate concentrations of 700-4000 ppm. Data has been collected to establish that the Cynoprobe is reliable and its measurements are accurate and reproducible for concentrations ranging from 5-155 ppm. The Cynoprobe's WAD cyanide reading produced an accuracy of greater than 90% with respect to laboratory methods; SFIA and FS laboratory ligand exchange.

The Cynoprobe's fast analysis time, of approximately 5 minutes for only free or WAD cyanide analysis, is suitable for use in control schemes and environmental monitoring. The Cynoprobe's free cyanide measurement has been used to show the benefits of automatic cyanide addition control over manual control, to achieve reagent savings, the results of which are beyond the scope of this thesis. Online WAD cyanide analysis facilitated tight cyanide destruction control with the Caro's acid process at a gold plant in Australia. Finally, environmental discharge monitoring of WAD cyanide concentrations as low as 0.3 ppm has proved invaluable for regulatory compliance at a plant in Africa.

To date, sixty seven Cynoprobe's have been installed across the globe. Of these, forty have been configured to measure WAD cyanide. Though the Cynoprobe's reputability is currently recognised by the leading gold mining houses, there is still on-going research and development required to resolve discrepancies between the various cyanide measurement techniques, to resolve interferences and to upgrade the hardware to include latest technology. The results of experiments conducted to compare the Cynoprobe's free cyanide measurement in the presence of copper and zinc to that of other free cyanide analysis techniques were beyond the scope of this thesis (van der Merwe and Breuer, 2011). However, at an applied potential of 0 mV, the Cynoprobe readings best correlated with the actual cyanide available to leach gold, that is the cyanide ion and the fourth and third cyanide bound to copper (see Section 2.2.3). This requires further investigation using a gold working electrode. The effect of temperature on the amperometric response for free cyanide concentrations ranging from 0.4-3800 ppm is currently being investigated with the objective of developing a temperature compensation algorithm. This will replace temperature control using heating pads which have required high maintenance. A continuous matrix separation analyser is also currently being developed to measure low free, WAD and Total cyanide concentrations, suitable for river discharge, ranging from 10-500 ppb.

REFERENCE LIST

Atkins, P.W., 1998. Physical Chemistry 6th ed. Oxford University Press, Oxford pp. 886-889

ABSCIEX Technology, 2011. Defining lower limits of quantification. [online]. Available at: <http://www.absciex.com> [Accessed 29 June 2011].

APHA 4500-CN^-, 1999. Inorganic Nonmetals (4000), Cyanide. American Public Health Association, Washington, DC, pp. 4.34-4.56.

ASTM D-2036-06, 2006. Standard Test Methods for Cyanides in Water. American Society for Testing and Materials International, West Conshohocken, United States of America.

ASTM D-4165-00, 2000. Standard Test Method for Cyanogen Chloride in Water. American Society for Testing and Materials International, West Conshohocken, United States of America.

ASTM D-4282-95, 1995. Standard Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion. American Society for Testing and Materials International, West Conshohocken, United States of America.

ASTM D-4374-93, 1993. Standard Test Methods for Cyanides in Water-Automated Methods for Total Cyanide, Dissociable Cyanide and Thiocyanate. American Society for Testing and Materials International, West Conshohocken, United States of America.

ASTM D-4374, 2006. Standard test methods for cyanides in water - automated methods for total cyanide, weak acid dissociable cyanide, and thiocyanate. American Society for Testing and Materials International, West Conshohocken, United States of America.

ASTM D-6696-05, 2006. Standard Guide for Understanding Cyanide Species. American Society for Testing and Materials International, West Conshohocken, United States of America.

ASTM D-6888-04, 2004. Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilising Gas Diffusion Separation and Amperometric Detection. American Society for Testing and Materials International, West Conshohocken, United States of America.

ASTM D-7237-06, 2006. Standard Test Method for Aquatic Free Cyanide with Flow Injection Anlaysis (FIA) Utilising Gas Diffusion Separation and Amperometric Detection. American Society for Testing and Materials International, West Conshohocken, United States of America.

Australian Academy of Science. 2012. Monitoring the white death – soil salinity. [online]. Available at: http://www.science.org.au [Accessed 8 March 2012].

Bark, L.S. and Higson, H.G., 1963. A review of Methods Available for the Detection and Determination of Small Amounts of Cyanide. Analyst 88, 751-760.

Barker, I J. 2007. The measurement of high cyanide concentrations in the Cynoprobe. Mintek Internal Report 40182

Barnes, D., Wright, P.J., Graham, S.M. and Jones-Watson, E.A., 2000. Techniques for the determination of Cyanide in a Process Environment: A review. The Journal of Geostandards and Geoanalysis, 24 (2), 183-195.

Botz, M.M., 2001. Overview of Cyanide Treatment Methods. [leaflet]. Elbow Creek Engineering, Inc. Montana, Wyoming, United States of America.

Breuer, P., Dai, X. and Jeffrey, M., 2005. Leaching of gold and copper minerals in cyanide deficient copper solutions. Hydrometallurgy, 94 (3-4), 156-165.

Breuer, P. and Hendersen, P., 2010. Online cyanide measurement and control for complex ores. In: ALTA 2010 Conference Proceedings, Gold Symposium. Perth, Western Australia 24-30 May 2010.

Breuer, P. and Rumball, J.A., 2007. Cyanide measurement and control for complex ores and concentrates. In: Ninth Mill Operators Conference, Fremantle, Western Australia March 2007. Carlton, Victoria, Australia, AusIMM. 249-254.

Breuer, P., Sutcliffe, C., Meakin, R., 2011. Cyanide measurement by silver nitrate titration: Comparison of rhodanine and potentiometric end-points. Hydrometallurgy, 106, 135-140.

Budapest Times, 2010. Hungary urges Europe-wide ban on cyanide mining technology. [online] (Last updated 02 February 2010) Available at: <http://www.budapesttimes.hu> [Accessed 9 September 2011].

Byegard, J., Skarnemark, G., Skalberg, M. 1999. The stability of some metal EDTA, DTPA and DOTA complexes: application aas tracers in groundwater studies. Radioanalytical and nuclear chemistry, 241 (2), 281-290.

Canterford, D.R., 1975. Simultaneous determination of cyanide and sulphide with rapid direct current polarography. Analytical Chemistry, 47, 88-92.

Chaize, T., 2011. World production of gold. [online] Available at: <http://www.dani2989.com/gold/goldproduction2011gb.html> [Accessed 28 June 2011] and USGS Historical statistics, Yearly Gold Production in metric tonnes (1900-2006). [online] Available at: <http://www.goldsheetlinks.com/production2.htm > [Accessed 28 June 2011].

Crundwell, F.K. and Jensen, J.O., 1994. An amperometric instrument for the determination of cyanide on gold plants. The Journal of the South African Institute of Mining and Metallurgy, 103-108.

CyPlus®, 2011. CyPlus® CCS - Cyanide Control System. [online]. Available at: <http://www.cyplus.com> [Accessed 9 September 2011].

DIN 38405 Part 13, 1981. Determination of Cyanides (D 13). German Standard Methods for the Analysis of Water, Waste Water and Sludge. German Standards, Berlin, Germany.

Dow Chemical Company 1995-2012. Brochures, technical and safety data sheets for ethyleneamines. [online]. Available at: <http://www.dow.com/amines> [Accessed 10 February 2012].

EPA Method 335.3, 1978. Cyanide, Total (Colorimetric, Automated UV). United States

Environmental Protection Agency, Washington DC, United States of America.

EPA Method 9010, 2004. Total and Amenable cyanide: distillation. United States Environmental Protection Agency, Washington DC, United States of America.

EPA Method 9014, 1996. Titrimetric and manual spectrophotometric determinative methods for cyanide. United States Environmental Protection Agency, Washington DC, United States of America.

EPA Method 9213, 1996. Potentiometric determination of cyanide in aqueous samples and distillates with ion-selective electrode. United States Environmental Protection Agency, Washington DC, United States of America.

EPA Method OIA-1677, 1999. Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry. United States Environmental Protection Agency, Washington DC, United States of America.

Fries, J. and Getrost, H., 1977. Organic Reagents for Trace Analysis. E Merck Darmstadt.

Gattrell, M., Cheng, S.C., Guena, T. and MacDougall, B., 2001. Cyanide ion selective electrode measurements in the presence of copper. J. Electroanal. Chem. 508, 97–104.

Gold Metallurgy. 2012. Refractory gold. [online]. Available at: <http://www.goldmetallurgy.com/refractory-gold> [Accessed 21 February 2012].

Hancock, P. and Skinner, B.J. 2000. The Oxford companion to the earth. [online]. Available at: <http://www.encyclopedia.com/doc/1O112-goldsilverandcopperdepsts.html> [Accessed 4 November 2011]

Harvey, D., 2000. Modern Analytical Chemistry. McGraw-Hill Companies, Inc. United States of America. Pp. 95-96.

Henze, T.G., 2001. Introduction to voltammeric analysis – theory and practice. CSIRO Publishing,

Collingwood VIC, Australia

Hewitt, D.M., Breuer P.L.*, Jeffrey, M.I. and Naim, F., 2009. Mechanisms of sulfide ion oxidation during cyanidation. Part II: Surface catalysis by pyrite. Minerals Engineering 22, 1166–1172.

Huntsman International Corporation. 2001-2012. Brochures and technical bulletins for ethyleneamines. [online]. Available at: <http://huntsman.com> [Accessed 10 February 2012].

Iamarino, P.F., 1989. The Direct Spectrophotometric Determination of Cyanide with Picric Acid Reagent. JRGRL. 1 June, 1989.

International Cyanide Management Institute, 2011. The International Cyanide Management Code. [online] Available at: <http://www.cyanidecode.org> [Accessed 16 August 2011].

International Mining, 2010. European Commission rejects proposed ban on using cyanide in extractive industry. [online] (Updated 6 July, 2010) Available at: <http://www.im-mining.com> [Accessed 9 September 2011].

ISO 6703-2, 1984. Water quality — Determination of cyanide — Part 2: Determination of easily liberatable cyanide 90.93 TC 147/SC 2. The International Organisation for Standardisation, Geneva, Switzerland.

Klein, B., 2001. Review of Cyanidation Technology in the Gold Mining Industry. [Course leaflet] 2001 ed. Prepared for: CDG/Wits Environmental Technology Assessment Training workshop in South Africa. Mining and Mineral Process Engineering, University of British Columbia, Canada.

Logsdon, M. J., Hagelstein, K. and Mudder, T. I., (1999). The Management of Cyanide in Gold Extraction. International Council on Metals and the Environment.

Lorösch, J., 2001. Process and Environmental Chemistry of Cyanidation. Degussa AG, Weissfrauenstrasse 9, D-60311 Frankfurt am Main, pp. 83-149, 259-263, 395-396, 427-468.

Lotz, P., 2001. Cyanide Technology and its application in the Mining Sector. [Course notes]

Prepared from: CDG/Wits Environmental Technology Assessment Training workshop in South Africa.

Lurje, J.J., 1971. Handbook of Analytical Chemistry, Chemistry, Moscow, pp. 265.

Maqsood, Z.T., Gulzar, S. and Fatima, N., 2002. Comparative study of polyaminocarboxylic acid complexes of essential and biotoxic metals. Journal of the Chemical Society of Pakistan, 24 (4), 262-264.

Marsden, J. O. and House, C. I., 2006. The Chemistry of Gold Extraction. 2nd ed. Society for Mining, Metallurgy and Exploration, Inc., pp. 234-271.

Mc Closkey, J.A., 1961. Direct amperometry of cyanide at extreme dilution. Analytical Chemistry, 33, (13), 1842-1843.

Mudder, T., 2007. Technical Statement Regarding Cyanide. Terry I. Mudder Environmental Services Ltd., Wyoming, United States of America.

Naumann, R., Weber, C. and Fresenius, Z., 1971. Titration von sulfidmit einer sulfidionensensitiven elekrode. Anal. Chem. 253, 111.

Nicol, M.J., 2010. Hydrometallurgy Theory and Practice. [Course notes]. Prepared for: UCT MSc course in Hydrometallurgy 2010-2011. Murdoch University, Perth, Western Australia.

OI Analytical, 2012. Flow Solution® FS 3100. [online]. Available at: http://oianalytical.com [Accessed 24 April 2012].

Orica Chemcials, 2011. OCM5000 Free Cyanide Analyser. [online]. Available at: <http://www.oricachemicals.com> [Accessed 9 September 2011].

Pihlar, B. and Kosta, L., 1979. Determination of Cyanides by Continuous Distillation and Flow Analysis with Cylindrical Amperometric Electrodes. Analytical Chimica Acta, 114, 275-281.

Poljanski, N.G. 1986. Analytical chemistry of elements. Led., Moscow, Science.

Pohlandt, C., Jones, E.A and Lee, A.F. 1983. A critical evaluation of methods applicable to the determination of cyanides. J. S. Afr. Inst. Min. Metall. 83, 11-17.

Process Analytic Process Analytical Systems (Pty) Ltd, 2011. TAC 1000 Cyanide & pH Analyser and controller, [online]. Available at: <http://www.process-analytical.co.za> [Accessed 9 September 2011].

Rainforest Information Centre, 2005. Cyanide Bans Worldwide. [online] (Last updated 24 July, 2005) Available at: <http://www.rainforestinfo.org.au/gold/Bans.html> [Accessed 28 June 2011].

Rodriguez, L. and Macias, F., 2009. To Cyanide or Not to Cyanide? Some Argentinean Provinces Banned Use of Cyanide in Mining Activities: Is this Prohibition Legal? Rocky Mountain Mineral Law Foundation Journal, 46 (2), 237-249.

SABS Method 204. 1981. Cyanide Content of Water. Council of the South African Bureau of Standards, Pretoria, South Africa.

SANS/ISO 14403, 2002. Water quality-Determination of total cyanide and free cyanide by continuous flow analysis. The International Organisation for Standardisation, Geneva, Switzerland.

Sato, T. 1989. Liquid-liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds. Hydrometallurgy, 22, 121-140.

Settle, F. 1997. Handbook of Instrumental Techniques for Analytical Chemistry (1st edition). Prentice Hall.

Shriver, D.F., Atkins, P.W. and Langford, C.H., 1994.Inorganic Chemistry second edition. Oxford University Press, Oxford pp. 227-241

Sillen, L.G. and Martell, A.E., 1964. Stability Constants of Metal Ion Complexes, The Chemical

Society, London, Special Publication, No. 17.

Sillen, L.G. and Martell, A.E., 1970. Stability Constants of Metal Ion Complexes. The Chemical Society, London, Special Publication, No. 25.

Singh, H.B. and Wasi, N., 1986. Detection and determination of cyanide – a review. Intern. J. Environmental Chem., 26, 115-136.

Smith, R.M. and Martell A.E., 1976. Critical Stability Constants. Volume 4. Plenum Press, New York.

Smith, A. and Mudder, T. 1991. The Chemistry and Treatment of Cyanidation Wastes. Mining Journal Books Ltd., P.O. Box 10, Edenbridge, Kent TN8 5NE, United Kingdom.

Tschugaeff, L. 1905. Über ein neues, empfindliches Reagens auf Nickel. Berichte der deutschen chemischen Gesellschaft, 38 (3), 2520–2522.

van der Merwe, W. and Breuer, P. 2011. Cyanide analysis for complex cyanide solutions. World Gold Conference 2011, Montreal, Canada, October 2011, CIM.

Visual MINTEQ. 2010. Visual MINTEQ ver. 3.0. [online]. Available at: <http://www2.lwr.kth.se/English/OurSoftware/vminteq/> [Accessed 19 September 2012].

Wikipedia, 2010. Wastewater discharge standards in Latin America. [online] (Updated 11 July 2011) Available at: <http://en.wikipedia.org> [Accessed 9 September 2011].

Yarar, B., 2002. Long term persistence of cyanide species in mine waste environments. Collorado School of Mines, Tailings and Mine Waste - Swets & Zeitlinger.

Young, C.A. and Jordan, T. S., 1995. Cyanide Remediation: Current and Past Technologies. In: Proceedings of the 10th Annual Conference on Hazardous Waste Research. Kansas State University, Manhattan, Kansas 23-24 May 1995.

APPENDIX A

Metal concentrations in plant solutions

Table A.1 ICP (Inductively Coupled Plasma) multi-metal analysis on leach and residue filtrates from Witwatersrand basin gold plants

Metal	Witwatersrand gold plant No.1 - 7th Leach Tank	Witwatersrand gold plant No.1 - CIP Residue	Witwatersrand gold plant No. 2 - CIP residue	Witwatersrand gold plant No.3 - Backfill filtrate	Witwatersrand gold plant No. 4 - CIL residue
Cu	13.00	4.30	8.70	0.70	11.00
Ni	7.60	7.50	1.61	0.50	0.40
Zn	<2	3.20	0.16	0.040	0.27
Ag			<0.02	1.40	0.39
Cd			<0.02	<0.02	<0.02
Pb	5.40	6.50	<0.02	<0.02	<0.02
Fe	45.00	<2	1.60	0.14	<0.02
Co	9.20	6.20	0.48	0.020	0.49
As	3.10	9.40	<0.02	0.29	0.12
Mo	6.50	5.80	<0.02	<0.02	<0.02
Mn	<2	<2	<0.02	0.035	<0.02
SO_4	351	272	635	739	509

Table A.2 ICP (Inductively Coupled Plasma) multi-metal analysis and chloride analysis on leach and residue filtrates from Australian gold plants

Metal	Aus. gold plant No.1 - CIL Tank (ppm)	Aus. gold plant No.2 - CIL Tank (ppm)	Aus. gold plant No.3 – CIL Tank 1 (ppm)	Aus. gold plant No.3 – CIL Tails (ppm)	Aus. gold plant No.4 – CIL Tank 1 (ppm)	Aus. gold plant No.4 – CIL Tails (ppm)	Aus. gold plant No.5 – CIL Tank 2 (ppm)	Aus. gold plant No.5 – CIL Tank 7 (ppm)
Cu	41.30*	9.70#	3.70	2.90	1.30#	1.10#	16.00	26.00
Ni	0.50*	<0.02#	8.40	7.40	<0.02#	0.14#	2.50	2.60
Zn	5.90*	0.50#	0.50	0.27	0.46#	0.55#	0.92	0.30
Ag	0.20*	3.20#	0.63	<0.02	0.28#	<0.02#	0.48	0.13
Cd	<0.02*	<0.02#	<0.02	<0.02	<0.02#	<0.02#	<0.02	<0.02
Pb	<0.02*	<0.02#	<0.02	<0.02	<0.02#	<0.02#	<0.02	<0.02
Fe	<0.02*	<0.02#	<0.02	<0.02	3.10#	14.00#	<0.02	<0.02
Co	0.10*	0.10#	0.80	0.80	0.19#	0.20#	<0.02	<0.02
As	<0.02*	<0.02#	0.32	<0.02	0.79#	<0.02#	0.37	0.39
Mo	0.40*	0.50#	0.12	0.06	<0.02#	<0.02#	0.64	0.68
Mn	<0.02*	<0.02#	<0.02	<0.02	<0.02#	0.08#	<0.02	<0.02
SO_4^{2-}	278*	1785#	3620	3200	3945#	3940#	5360	5840
Cl^-	440*	180#	321	304	267#	273#	702	691

*Average of three samples, #Average of two samples.

APPENDIX B

Chemical modelling of cyanide systems

Figure B.1 Screen shot of Mintek Cyanide Centre speciation spread-sheet

REPORT SHEET - CYANIDE SPECIATION & ANALYSIS FOR LIQUID SAMPLE

Sample no.:	**Wits DBM project**					
Processed by:	Welhem	Date received:				
pH:	10.50	Eh (vs SHE):	-270 mV	**conductivity:**	6.56 mS/cm	

	computed detailed speciation			**metal based sums**	
species	**CN, ppm individual species**	*% CN as*	% total metal	**CN: total per metal in ppm**	**metal analysis, ppm**
$[Fe(CN)_6]^{4-}$	**11.73**	*3.2*	100.00	**11.73**	**4.201**
$[Fe(CN)_5]^{3-}$	**0.**	*0.0*	0.00		
$[Cu(CN)_2]^-$	**0.03**	*0.0*	0.07		
$[Cu(CN)_3]^{2-}$	**53.69**	*14.7*	88.44	**63.01**	**49.458**
$[Cu(CN)_4]^{3-}$	**9.3**	*2.5*	11.49		
$[Co(CN)_6]^{3-}$	**4.52**	*1.2*	100.00	**4.52**	**1.706**
$[Zn(CN)_2]$	**0.**	*0.0*	0.00		
$[Zn(CN)_3]^-$	**0.05**	*0.0*	2.53		
$[Zn(CN)_4]^{2-}$	**2.77**	*0.8*	97.38	**2.83**	**1.788**
$[Zn(CN)_2OH]^-$	**0.**	*0.0*	0.00		
$[Zn(CN)_3OH]^{2-}$	**0.**	*0.0*	0.09		
Zn^{2+}, ZnOH's etc.	**0.**	*0.0*	0.00		
$[Ni(CN)]^+$	**0.**	*0.0*	0.00		
$[Ni(CN)_2]$	**0.**	*0.0*	0.00		
$[Ni(CN)_3]^-$	**0.**	*0.0*	0.00	**0.83**	**0.468**
$[Ni(CN)_4]^{2-}$	**0.83**	*0.2*	99.79		
$[Ni(CN)_5]^{3-}$	**0.**	*0.0*	0.21		

CN^-	268.31	*73.5*	Deviation:	***Confirming analysis:***	
HCN (aq)	**13.761**	*3.8*	%	ppm CN	method
Free CN	**282.071**	*77.3*	-2.6%	275.	◂ ISE (corrected) [1]
Titratable CN	**287.22**	*78.7*	15.5%	340.	◂ $AgNO_3$ pot. Tit.
Gold leachable CN	307.26	*84.2*			
WAD CN	**348.741**	*95.5*	-2.2%	341.	◂ SFIA
Total CN	**365.**	*100.0*	-4.7%	348.	◂ SFIA [2]
Total CN + [S]CN	**365.**			365.	◂ SFIA [3]
CN ex SCN	**0.**				
CN ex SCN (SCN=x2.23!)	**ND**	◂ Ion Chrom.	#VALUE!	Δ SFIA	

[1] CN ISE has been corrected for over-estimation due to Zn; no correction for significant figures post calculation.

[2] CN Total has been corrected for the partial recovery of cyanide from $Au(CN)_2$ and $Co(CN)_6$; it has not been corrected for significant figures post re-calculation. ISE= Ion Selective Electrode, SFIA = Segemented Flow Iniection Analysis

[3] This quantity captures CN Total as well as the CN component of SCN. The actual SCN value is calculated to be : --> 0. ppm

Table B.1 Theoretical speciation of copper cyanide solutions, at pH 12 and 25ºC determined using Mintek speciation spread-sheet

Species	Concentration (ppm)				
	100 ppm WAD CN	50 ppm WAD CN	25 ppm WAD CN	10 ppm WAD CN	0.5 ppm WAD CN
Total Cu	61.06	30.53	15.26	6.11	0.30
$[Cu(CN)_2]^-$	0.41	0.40	0.39	0.36	0.13
$[Cu(CN)_3]^{2-}$	73.45	36.65	18.09	6.95	0.18
$[Cu(CN)_4]^{3-}$	1.18	0.30	0.08	0.01	0.00
CN^-	24.93	12.63	6.44	2.68	0.19
$HCN_{(aq)}$	0.04	0.02	0.01	0.00	0.00
Free CN	24.97	12.65	6.45	2.68	0.19
Titratable CN	25.26	12.73	6.46	2.68	0.19
Gold leachable CN	49.79	24.90	12.45	4.98	0.25
WAD CN	100.00	50.00	25.00	10.00	0.50
Total CN	100.00	50.00	25.00	10.00	0.50

Table B.2 Theoretical speciation of nickel cyanide solutions, at pH 12 and 25ºC determined using Mintek speciation spread-sheet

Species	Concentration (ppm)				
	100 ppm WAD CN	50 ppm WAD CN	25 ppm WAD CN	10 ppm WAD CN	0.5 ppm WAD CN
Total Ni	56.39	28.20	14.10	5.64	0.28
$[Ni(CN)]^+$	0.00	0.00	0.00	0.00	0.00
$[Ni(CN)_2]$	0.00	0.00	0.00	0.00	0.00
$[Ni(CN)_3]^-$	0.31	0.24	0.18	0.12	0.03
$[Ni(CN)_4]^{2-}$	99.49	49.69	24.73	9.83	0.46
$[Ni(CN)_5]^{3-}$	0.00	0.00	0.00	0.00	0.00
CN^-	0.20	0.13	0.09	0.05	0.01
$HCN_{(aq)}$	0.00	0.00	0.00	0.00	0.00
Free CN	0.20	0.13	0.09	0.05	0.01
Titratable CN	0.20	0.13	0.09	0.05	0.01
Gold leachable CN	0.20	0.13	0.09	0.05	0.01
WAD CN	100.00	50.00	25.00	10.00	0.50
Total CN	100.00	50.00	25.00	10.00	0.50

Table B.3 Theoretical speciation of zinc cyanide solutions, at pH 12 and 25ºC determined using Mintek speciation spread-sheet

Species	Concentration (ppm)				
	100 ppm WAD CN	50 ppm WAD CN	25 ppm WAD CN	10 ppm WAD CN	0.5 ppm WAD CN
Total Zn	62.85	31.42	15.71	6.29	0.31
$[Zn(CN)_2]$	0.04	0.02	0.01	0.00	0.00
$[Zn(CN)_3]^-$	7.70	3.25	0.98	0.07	0.00
$[Zn(CN)_4]^{2-}$	48.89	16.18	3.57	0.13	0.00
$[Zn(CN)_2OH]^-$	1.85	0.99	0.41	0.06	0.00
$[Zn(CN)_3OH]^{2-}$	8.29	3.50	1.06	0.08	0.00
Zn^{2+}, ZnOH's etc.	0.00	0.00	0.00	0.00	0.00
CN^-	33.17	26.01	18.94	9.65	0.50
$HCN_{(aq)}$	0.05	0.042	0.03	0.02	0.00
Free CN	33.23	26.05	18.97	9.67	0.50
Titratable CN	100.00	50.00	25.00	10.00	0.50
Gold leachable CN	100.00	50.00	25.00	10.00	0.50
WAD CN	100.00	50.00	25.00	10.00	0.50
Total CN	100.00	50.00	25.00	10.00	0.50

Table B.4 Theoretical speciation of silver cyanide solutions, at pH 12 and 25ºC determined using Mintek speciation spread-sheet

Species	Concentration (ppm)				
	100 ppm WAD CN	50 ppm WAD CN	25 ppm WAD CN	10 ppm WAD CN	0.5 ppm WAD CN
Total Ag	207.28	103.64	51.82	20.73	1.04
$[Ag(CN)_2]^-$	99.92	49.96	24.98	9.99	0.50
$[Ag(CN)_3]^-$	0.01	0.00	0.00	0.00	0.00
CN^-	0.08	0.04	0.02	0.01	0.00
$HCN_{(aq)}$	0.00	0.00	0.00	0.00	0.00
Free CN	0.08	0.04	0.02	0.01	0.00
Titratable CN	0.08	0.04	0.02	0.01	0.00
Gold leachable CN	0.08	0.04	0.02	0.01	0.00
WAD CN	100.00	50.00	25.00	10.00	0.50
Total CN	100.00	50.00	25.00	10.00	0.50

Table B.5 Theoretical speciation of combination metal cyanide solutions (40% free CN, 40% Cu-CN, 20% Ni-CN), at pH 12 and 25ºC determined using Mintek speciation spread-sheet

Species	Concentration (ppm)			
	100 ppm WAD CN	50 ppm WAD CN	10 ppm WAD CN	0.5 ppm WAD CN
Total Cu	24.42	12.21	2.44	0.12
$[Cu(CN)_2]^-$	0.08	0.08	0.08	0.04
$[Cu(CN)_3]^{2-}$	29.15	14.69	2.87	0.09
$[Cu(CN)_4]^{3-}$	0.94	0.24	0.01	0.00
Total Ni	11.28	5.64	1.13	0.06
$[Ni(CN)]^+$	0.00	0.00	0.00	0.00
$[Ni(CN)_2]$	0.00	0.00	0.00	0.00
$[Ni(CN)_3]^-$	0.00	0.00	0.00	0.00
$[Ni(CN)_4]^{2-}$	19.97	9.99	2.00	0.10
$[Ni(CN)_5]^{3-}$	0.01	0.00	0.00	0.00
CN^-	49.77	24.96	5.03	0.27
$HCN_{(aq)}$	0.08	0.04	0.01	0.00
Free CN	49.85	25.00	5.04	0.27
Titratable CN	50.08	25.06	5.04	0.27
Gold leachable CN	59.94	29.97	5.99	0.30
WAD CN	100.00	50.00	10.00	0.50
Total CN	100.00	50.00	10.00	0.50

APPENDIX C

Dynamic concentration ranges - potentiostat board v1.0 and v2.0

Figure C.1 **Potentiostat board v1.0 (10 000 Ω, 0-20 ppm, 35ºC, V_{sp} = -140 mV) - percent error and relative standard deviation**

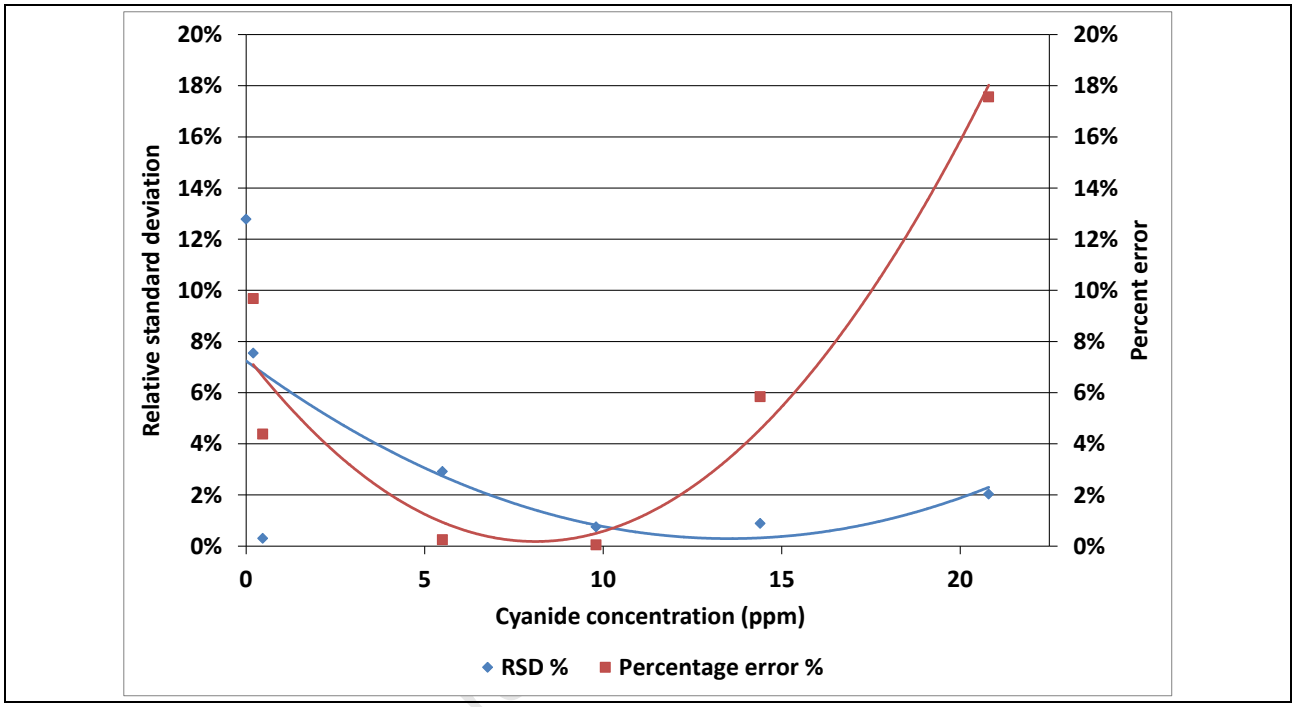


Figure C.2 **Potentiostat board v1.0 (1000 Ω, 0-200 ppm, 35ºC, V_{sp} = -140 mV) - percent error and relative standard deviation**

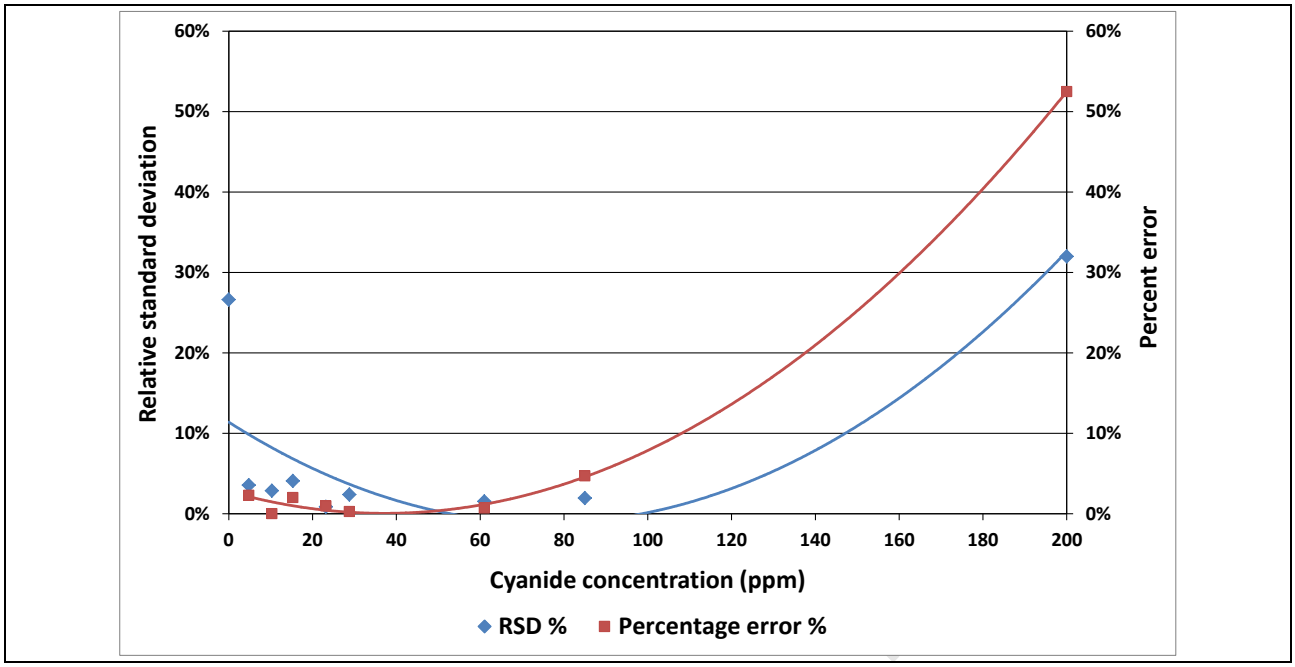


Figure C.3 **Potentiostat board v1.0 (500 Ω, 35ºC, V_{sp} = -140 mV) - percent error and relative standard deviation**

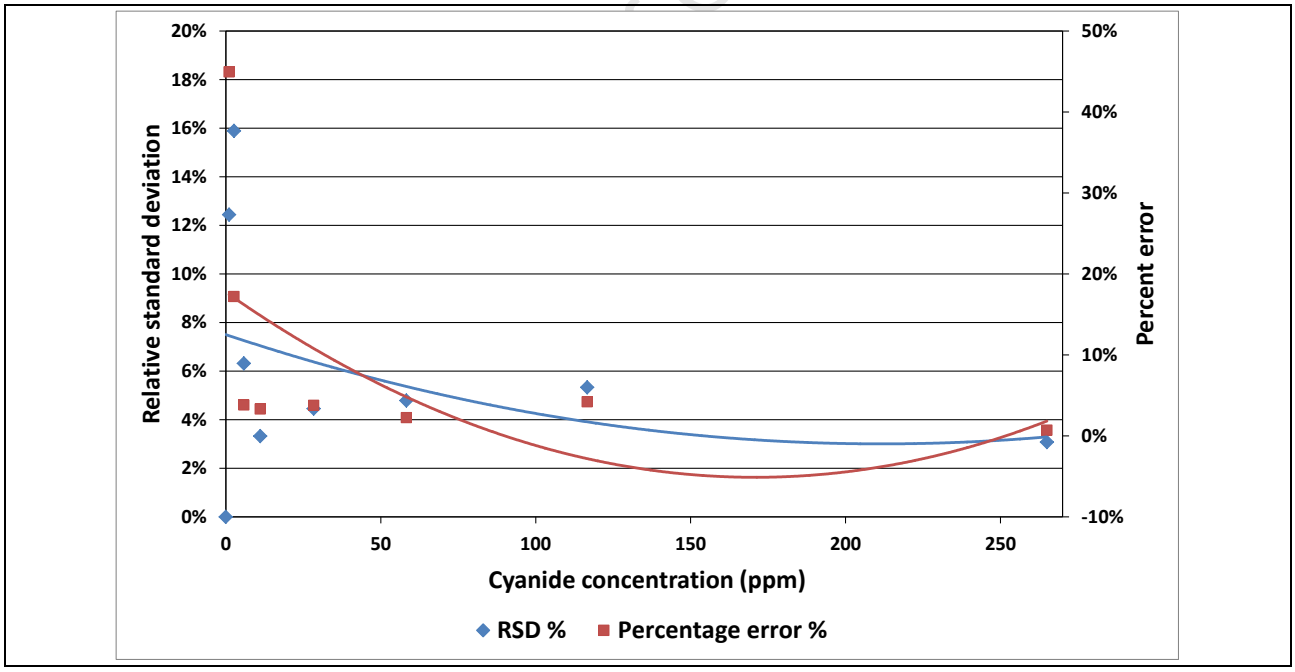


Figure C.4 **Potentiostat board v1.0 (100 Ω, 35ºC, V_{sp} = -140 mV) - percent error and relative standard deviation**

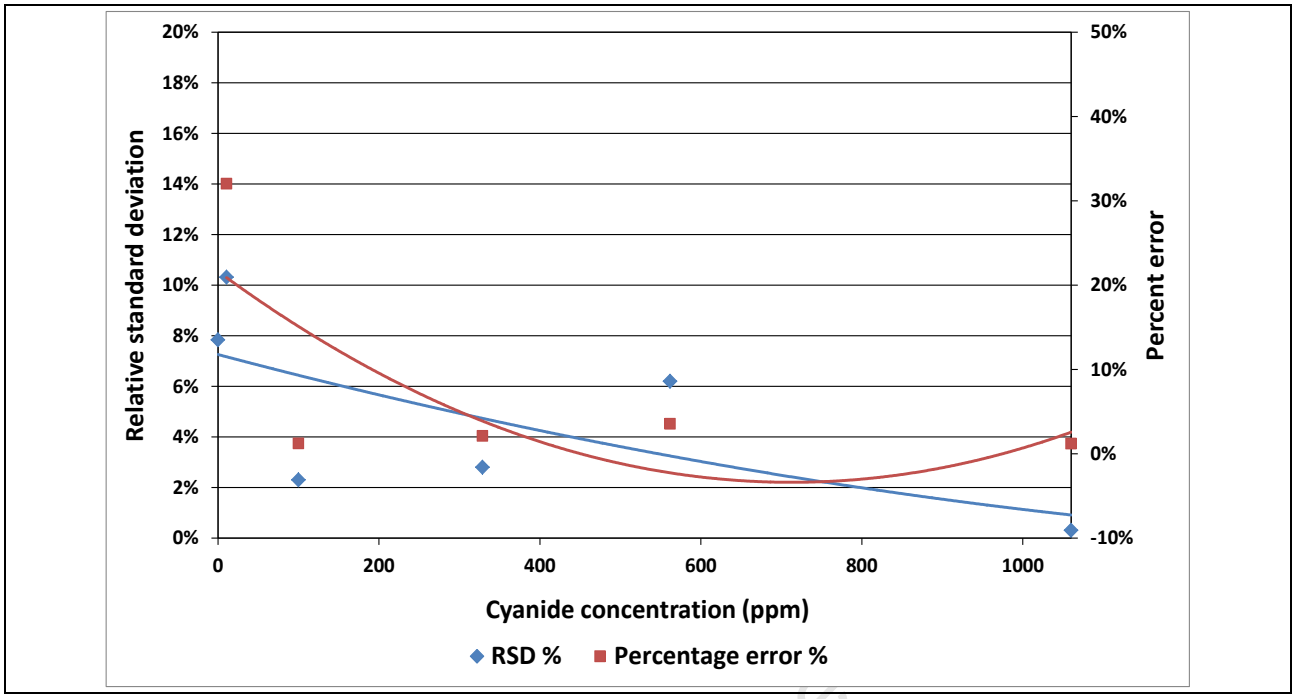


Figure C.5 **Potentiostat board v1.0 (10 Ω, 35ºC, V_{sp} = -140 mV) - percent error and relative standard deviation**

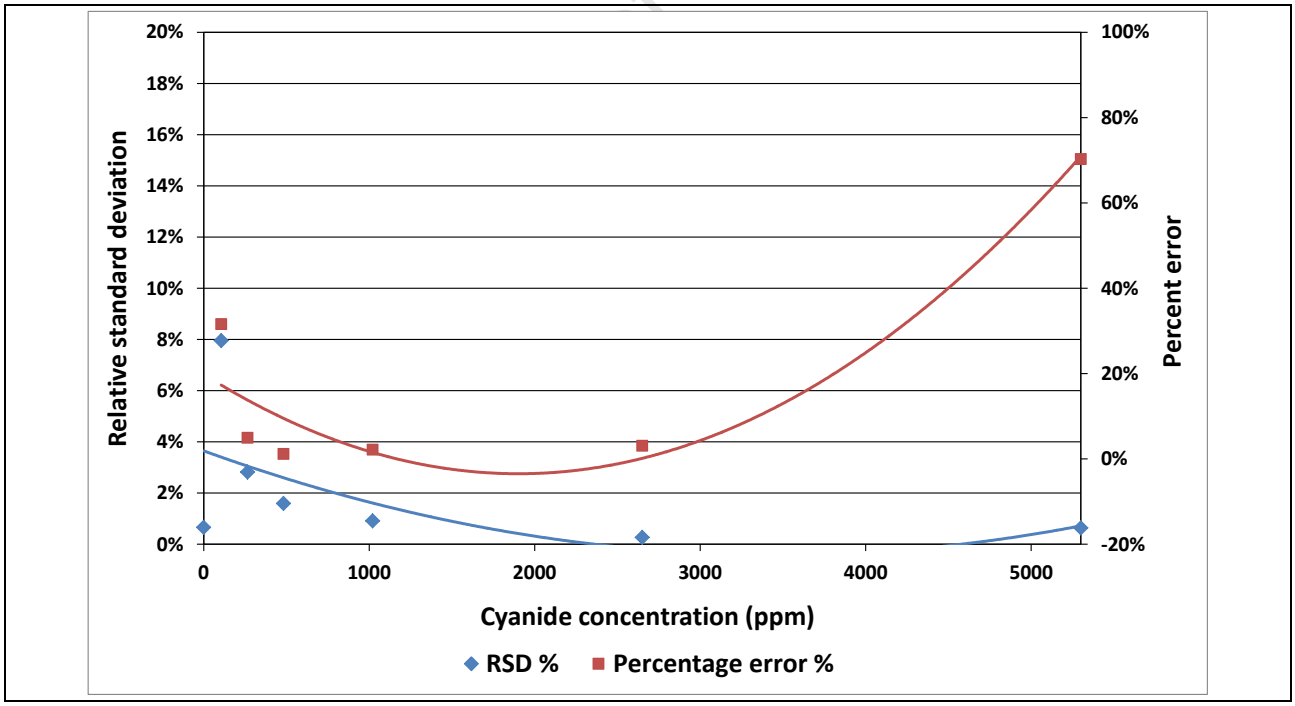


Figure C.6 **Potentiostat board v2.0 (4020 Ω, 35°C, V_{sp} = -140 mV) - percent error and relative standard deviation**

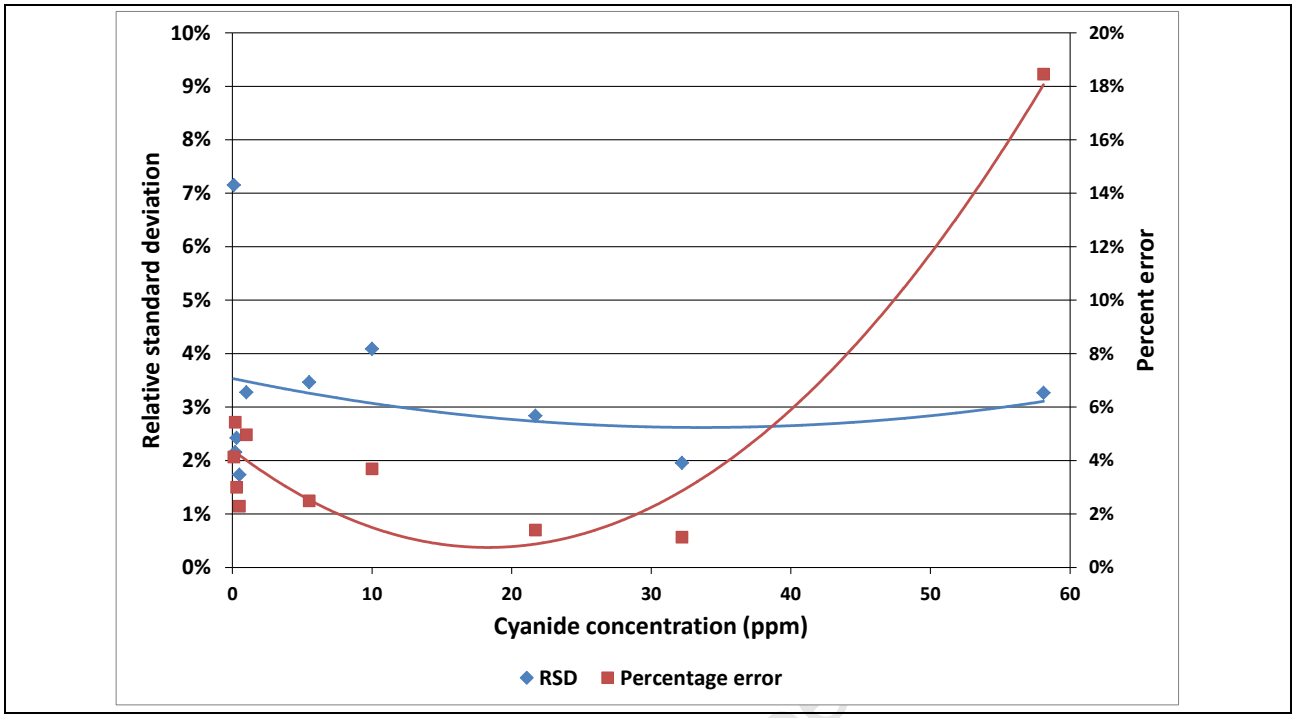


Figure C.7 **Potentiostat board v2.0 (1214 Ω, 35°C, V_{sp} = -140 mV) - percent error and relative standard deviation**

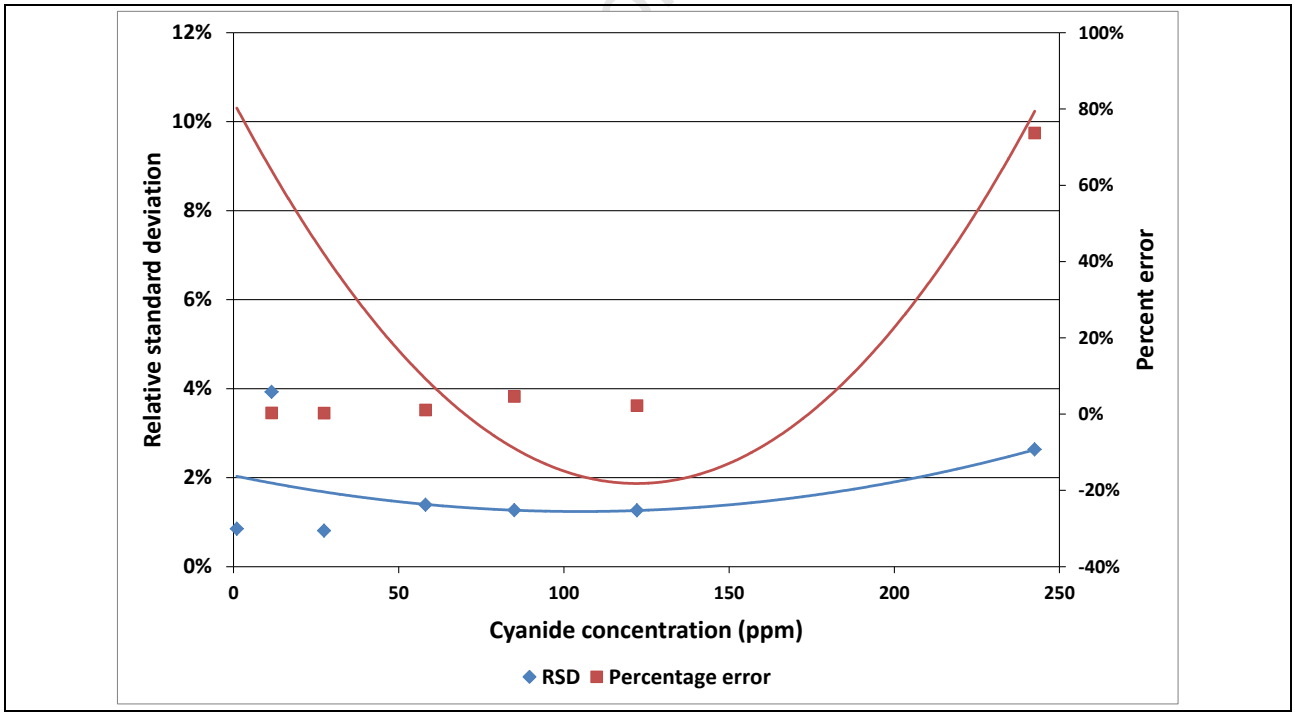


Figure C.8 **Potentiostat board v2.0 (354.2 Ω, 35ºC, V_{sp} = -140 mV) - percent error and relative standard deviation**

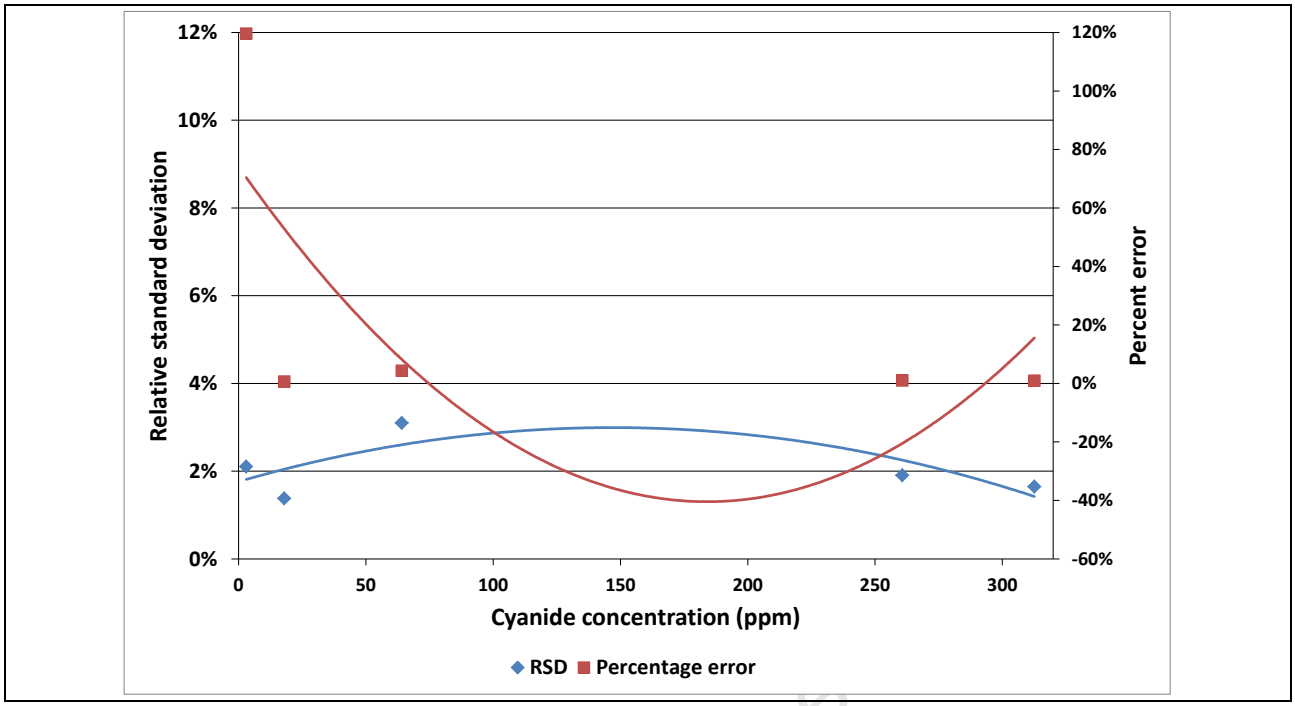


Figure C.9 **Potentiostat board v2.0 (117.1 Ω, 35ºC, V_{sp} = -140 mV) - percent error and relative standard deviation**

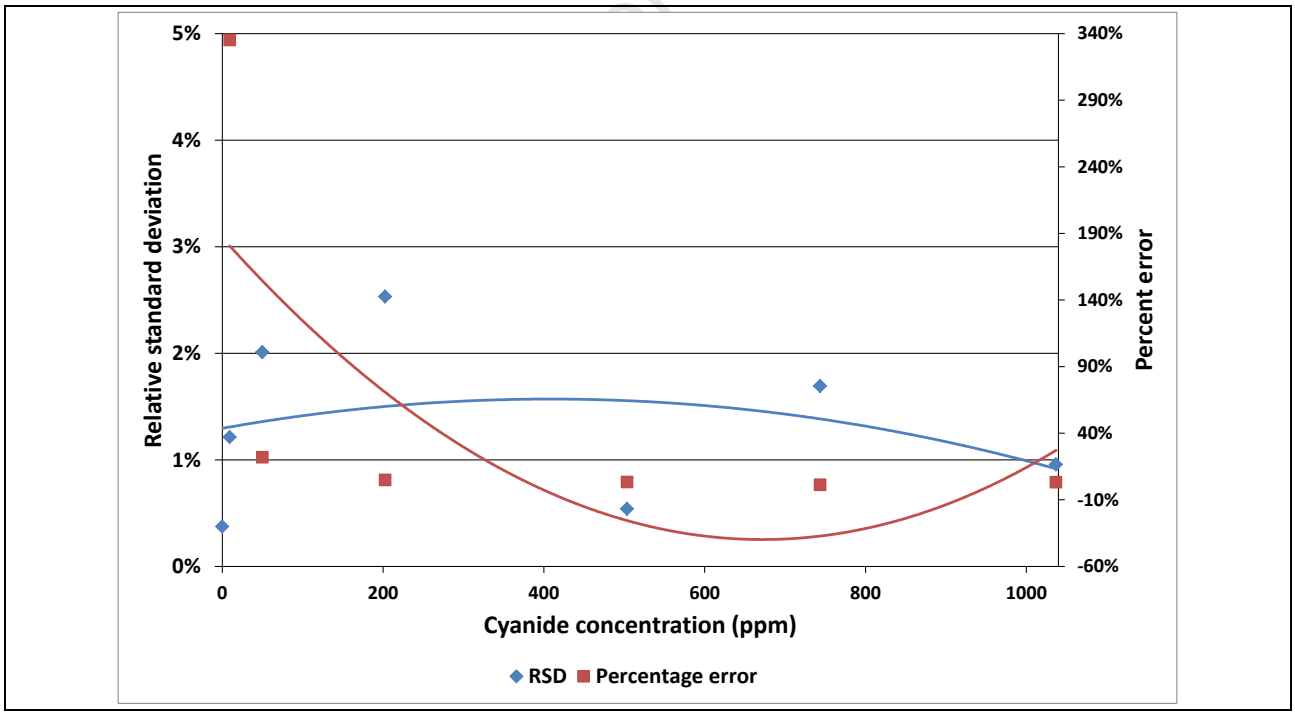


Figure C.10 **Potentiostat board v2.0 (40.75 Ω, 35ºC, V_{sp} = -140 mV) - percent error and relative standard deviation**