

**HYDROLYSIS AND CYANIDE SPECIATION OF SOME  
HEAVY METALS RELEVANT TO THE  
FATE OF CYANIDE IN THE ENVIRONMENT**

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*“Alam Hi Vō Kālāmā Kanthitum Alam Vicikicchitum,  
 Kankhanīyē Ca Pana Vō Thānē Vicikicchā Uppannā,  
 Etha Tumhē Kālāmā Mā Anussavēna,  
 Ma Paramparāya, Mā Itikirāya, Mā Pitaka Sampadānēna,  
 Mā Takkahētu, Mā Naya Hētu, Mā Ākāra Parivittakkena,  
 Mā Ditthi Nijjhanakkhantiyā, Mā Bhabharūpatāya,  
 Mā Samanō Nō Garūti. Yadā Tumhē Kālāmā,  
 Attanāva Jāneyyātha, Imē Dhammā Akusalā,  
 Imē Dhammā Sāvajjā, Imē Dhammā Viññū Garahitā,  
 Imē Dhammā Samattā, Samādinna Ahitāya Dukkāya  
 Samvattantiti: Atha Tumhē Kālāmā Pajaheyyātha.”*

Do not believe in anything (simply) because you have heard it.

Do not believe in traditions because they have been handed down for many generations.

Do not believe in anything because it is spoken and rumoured by many.

Do not believe in anything (simply) because it is found written in your religious books.

Do not believe in anything merely on the authority of your teachers and elders.

But after observation and analysis, when you find something agrees with reason and is conducive to the good and benefit of one and all, then accept it and live up to it.

**BUDDHA**  
*Kalama Sutta*  
*(Anguttara Nikaya Vol I, 188–193 P.T. S. Ed)*

**I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institution.**

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**Weeratunge Nimal Perera**

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## ABBREVIATIONS

A	Absorbance value
antilog	Exponential to the base of 10
$a^*$	Absorbance per $[M^{Z+}]_T$ and $\ell$ as defined in Equation 2.8
$a_{\text{species}}$	Activity of the species
atm	Pressure unit in atmospheres
$B_0$	External magnetic field
c	Concentration of species
D, D#, D'	Diffusion coefficients of the various species in $\text{cm}^2\text{sec}^{-1}$
$E^a, E^0$	Standard potentials at two different conditions
$E_J$	Energy difference between the nondegenerate nuclear spin states
$E_{\text{pulse}}$	Pulse potential in differential pulse polarography
$E_{1/2s}, E_{1/2c}$	Half-wave potentials of the simple and complexed metal ions in direct current polarography
$(E_p)_s, (E_p)_c$	Peak potentials of the simple and complexed metal ions in differential pulse polarography
F	Faraday's constant, $96485.309 \text{ Cmol}^{-1}$
$F_0(X)$	Function according to Equation 2.10
$F_n(X)$	Iterative function according to Equation 2.11
g	Gyromagnetic ratio
h	Planck's constant: $6.6260755 \times 10^{-34} \text{ J s}$
I	Ionic strength of the solution in moles per litre(M) corresponding to Equation 1.11

$I_p$	Peak current from a differential pulse polarograph
$(I_p)_c, (I_p)_s$	Peak currents of the complex and simple metal ions from a differential pulse polarograph
$i$	Current flowing into the mercury electrode
$i_d$	Diffusion controlled current flow
$J, J_N$	Total nuclear spin
$J_M$	Total nuclear spin of the adjoining atom in a ligand
$k, k\#, k$	Ilkovic constants of the various species
$K_H$	The Henry's Law constant in $\text{atm M}^{-1}$
$K_{1q}$	Stepwise formation constant of species $ML_q$ corresponding to Equation 1.15
$\ell$	Pathlength of the spectrophotometric cell
$\ln$	Natural logarithm (base $e$ ) (where $e$ is the Euler's constant)
$\log$	Logarithm to the base 10
$\log^*K_{sp}$	$\log$ of the solubility product according to Equation 2.17
$M$	Concentration in molarity <i>i.e.</i> moles per liter of solution
$[M(II)]_T$	Total metal concentration in solution
$m_i$	Concentration of the $i$ th ion in molalities <i>i.e.</i> moles per 1kg of solvent
$m_j$	Nuclear spin state
$N_c$	Number of ligands specified in the SPECFIT model
$n$	The number of electrons involved in the electrochemical reaction
$pH$	Negative logarithm (base 10) of $[H^+]$
$p$	Number of metal ions present in a particular species
$pK_w$	Negative log of the dissociation constant of water at 25°C



$pK_a$	Negative log of the dissociation constant of an acid in water at 25°C
$q$	Number of ligands present in a particular species
$R$	Ideal gas constant, $8.31451 \text{ JK}^{-1}\text{mol}^{-1}$
[species]	Concentration of the species in moles per litre (M)
$T$	Thermodynamic temperature in Kelvin (K)
$t$	Mercury drop time, seconds
$z_i$	Charge number of the $i$ th ion
$\beta, \beta_{pq}$	Stoichiometric formation constant corresponding to Equation 1.8
$*\beta_{pq}$	Stoichiometric formation constant corresponding to Equation 1.13
$\beta^0_{pq}$	Thermodynamic formation constant corresponding to Equation 1.9
$\Delta$	Difference in values
$\Delta E_p$	Difference between $(E_p)_s$ and $(E_p)_c$
$\varepsilon_\lambda$	Absorptivity at wavelength $\lambda$
$\gamma_i$	The activity coefficient of the $i$ th component
$\pi$	The pi constant: 3.14159
$\nu_i$	Stoichiometric coefficients of the $i$ th component
$\nu_i, \nu_{\text{ref}}, \nu_0$	Nuclear magnetic resonance frequency
$\sigma$	Experimental standard deviation

## ABSTRACT

Quantitative understanding of the fate of cyanide in the environment and its role in industrial processes requires quantitative characterisation of metal ion–cyanide complex formation and also the corresponding metal ion hydrolysis reactions that frequently compete with them. This thesis presents quantitative data for complex formation constants obtained using a range of techniques for a number of metal ion–hydroxide and metal ion–cyanide systems of environmental and hydrometallurgical importance that have been found difficult to study in the past. A specially–constructed combined spectrophotometric /potentiometric cell has enabled a variety of systems to be studied by UV–Visible spectroscopy at very low metal ion concentrations. This has circumvented problems associated with precipitation and/or polynuclear metal complex formation, which frequently predominate in these systems at higher concentrations.

Using this approach it has been possible to determine the formation constants and spectra of the mononuclear hydroxide complexes of Pb(II), Cu(II), Fe(III), Ag(I) and for the cyanide complexes of Pb(II), Ag(I), Ni(II) and Fe(III). It has also been possible to estimate the solubility products of  $\text{Pb}(\text{CN})_2(\text{s})$ ,  $\text{AgOH}(\text{s})$ ,  $\text{AgCN}(\text{s})$  and  $\text{NaFeFe}(\text{CN})_6(\text{s})$ . For some of these species (namely,  $\text{Pb}(\text{OH})_4^{2-}$ , the higher order hydroxo–complexes of Cu(II) and Fe(III),  $\text{Pb}(\text{CN})^+$ , and the lower cyano–complexes of Fe(III)), the present results are the first quantitative estimates of their formation constants. These complexes have long been assumed to exist on theoretical grounds but have proven difficult to quantify experimentally. The main reasons for this difficulty are the sparing solubility of

the neutral hydroxides and /or cyanides and the tendency of  $\text{CN}^-$  to form either very weak or extremely strong complexes.

Where possible, attempts were made to confirm the spectrophotometric results using other techniques such as polarography, NMR spectroscopy (for  $\text{Pb(II)}$ ), Raman spectroscopy and, for  $\text{Cu(II)}$ , ESR spectroscopy. However, although these techniques were sometimes able to provide useful insights into the nature of the species formed, in general they were not sufficiently sensitive, or suffered from other constraints that meant that they yielded little quantitative information.

The formation constants measured in this work were combined with literature data to model the chemical behaviour of hypothetical cyanide-infiltrated soil. This modelling indicates that under typical contaminated soil conditions (*i.e.* soil containing  $\text{Fe(OH)}_3(\text{s})$  and  $[\text{CN}^-] = 0.1\text{mM}$ ), cyanide will be present mainly as the various forms of Prussian blue. However, strong competition between cyanide and hydroxide ions for  $\text{Fe(III)}$ , points to possible conditions for the chemical degradation of the Prussian blue.