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# Cyanide ion-selective electrode measurements in the presence of copper

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**Abstract**

The response of a cyanide ion-selective electrode (ISE) in the presence of copper has been investigated. The interferences of metal ions, like copper, on the response of the cyanide ISE prevents its use for routine direct analysis of metal cyanide containing waste water. In this work an improved understanding of the chemistry at the electrode, and the effects of different cyanide and copper concentrations and matrix pH values on the electrode response, has been developed. Based on this insight, a semi-empirical approach is described to allow calibration of the ISE enabling the estimation of total cyanide. While not as robust as, for example, total cyanide distillation, it provides an inexpensive, rapid and convenient approach for more frequent and widespread screening of industrial waste waters. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Ion selective electrodes (ISE); Cyanide; Analysis of cyanide; Metal complexes; Equilibria

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## 1. Introduction

Copper cyanide solutions are encountered in working with copper plating and with waste water from some gold mines. In the particular case of gold mining waste water, there is a need to measure cyanide in solutions with a low cyanide to copper ratio (typically 3:1–8:1). Under these conditions, strong deviations are observed in the ISE response due to the influence of copper. Thus, for these solutions, it is usually recommended first to acidify the solutions to decompose the metal cyanide complexes, then complex the metal with EDTA, and then re-adjust to high pH before measuring the cyanide with the ISE [1]. Other approaches involve total cyanide distillation prior to reading with the ISE [2,3] or ion chromatography [4].

The influence of metal cyanide complexes on the ISE has been discussed by Mascini and Napoli [5]. The cyanide ISE relies on measuring the local activity of iodide at a silver iodide electrode surface generated by the following reaction:

$$\mathrm{AgI_{(s)}} + 2\mathrm{CN^-} \rightleftarrows \mathrm{Ag(CN)_2^-} + \mathrm{I^-} \quad K_0 = 2.1\times10^4 \quad [6] \tag{1}$$

This reaction depletes the local cyanide concentration at the electrode surface and so for the case of copper cyanide complexes, this reaction will be in equilibrium with:

$$\mathrm{Cu^+} + \mathrm{CN^-} \rightleftarrows \mathrm{CuCN} \quad K_1 = 8.7\times10^{14} \quad [7] \tag{2}$$

$$\mathrm{Cu^+} + 2\mathrm{CN^-} \rightleftarrows \mathrm{Cu(CN)_2^-} \quad K_2 = 1.0\times10^{24} \quad [7] \tag{3}$$

$$\mathrm{Cu^+} + 3\mathrm{CN^-} \rightleftarrows \mathrm{Cu(CN)_3^{2-}} \quad K_3 = 3.9\times10^{28} \quad [7] \tag{4}$$

(For the solutions used in this work the concentration of $[\mathrm{Cu(CN)_4}]^{3-}$ is negligible.)

Following the approach of Mascini and Napoli [5], when such a system is at equilibrium with the copper cyanide complexes, the following equations can be written for the total cyanide ($\mathrm{CN_T}$) and total metal ion ($\mathrm{M_T}$) concentrations:

$$\mathrm{CN_T} = 2[\mathrm{Ag(CN)_2^-}] + [\mathrm{CN^-}] + [\mathrm{CuCN}] + 2[\mathrm{Cu(CN)_2^-}] + 3[\mathrm{Cu(CN)_3^{2-}}] \tag{5}$$

$$\mathrm{M_T} = [\mathrm{Cu^+}] + [\mathrm{CuCN}] + [\mathrm{Cu(CN)_2^-}] + [\mathrm{Cu(CN)_3^{2-}}] \tag{6}$$

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Each copper cyanide complex concentration can be written in terms of its formation constant ($K_i$) and the concentrations of the metal ion and free cyanide. Also from the stoichiometry of Eq. (1), it is known that:

$$[\mathrm{Ag(CN)_2^-}] = [\mathrm{I^-}] \quad \text{thus } [\mathrm{CN^-}] = [\mathrm{I^-}]/K_0^{1/2} \tag{7}$$

and for a calibrated ISE, the reading ($\mathrm{CN_{ISE}}$) will be equal to:

$$\mathrm{CN_{ISE}} = 2[\mathrm{I^-}] \quad \text{thus } [\mathrm{CN^-}] = \mathrm{CN_{ISE}}/(2K_0^{1/2}) \tag{8}$$

combining together Eqs. (5), (7) and (8) yields:

$$\begin{aligned}\mathrm{CN_T} = \mathrm{CN_{ISE}} + \frac{\mathrm{CN_{ISE}}}{2K_0^{1/2}} + \frac{K_1[\mathrm{Cu^+}]\mathrm{CN_{ISE}}}{2K_0^{1/2}} \\ + \frac{K_2[\mathrm{Cu^+}]\mathrm{CN_{ISE}^2}}{2K_0} + \frac{3K_3[\mathrm{Cu^+}]\mathrm{CN_{ISE}^3}}{8K_0^{3/2}}\end{aligned} \tag{9}$$

and combining Eqs. (6)–(8) yields:

$$\begin{aligned}\mathrm{M_T} = [\mathrm{Cu^+}] + \frac{K_1[\mathrm{Cu^+}]\mathrm{CN_{ISE}}}{2K_0^{1/2}} + \frac{K_2[\mathrm{Cu^+}]\mathrm{CN_{ISE}^2}}{4K_0} \\ + \frac{K_3[\mathrm{Cu^+}]\mathrm{CN_{ISE}^3}}{8K_0^{3/2}}\end{aligned} \tag{10}$$

Eqs. (9) and (10) can be combined, eliminating the $[\mathrm{Cu^+}]$ term. Then, if the total metal ion concentration ($\mathrm{M_T}$) is known from some other measurement (such as HPLC or AA), the total cyanide can be calculated by:

$$\begin{aligned}\mathrm{CN_T} = \mathrm{CN_{ISE}}\left\{1 + \frac{1}{2K_0^{1/2}}\right\} \\ + \frac{\mathrm{M_T}\left\{\dfrac{K_1\mathrm{CN_{ISE}}}{2K_0^{1/2}} + \dfrac{K_2\mathrm{CN_{ISE}^2}}{2K_0} + \dfrac{3K_2\mathrm{CN_{ISE}^3}}{8K_0^{3/2}}\right\}}{\left\{1 + \dfrac{K_1\mathrm{CN_{ISE}}}{2K_0^{1/2}} + \dfrac{K_2\mathrm{CN_{ISE}^2}}{4K_0} + \dfrac{K_2\mathrm{CN_{ISE}^3}}{8K_0^{3/2}}\right\}}\end{aligned} \tag{11}$$

which can be simplified by noting that:

$$1 + \frac{1}{2K_0^{1/2}} \approx 1 \tag{12}$$

One can also evaluate the error ($\varepsilon$) of the ISE reading relative to the amount of copper ion present:

$$\begin{aligned}\varepsilon = \frac{\mathrm{CN_T} - \mathrm{CN_{ISE}}}{\mathrm{M_T}} \\ = \frac{\left\{\dfrac{K_1\mathrm{CN_{ISE}}}{2K_0^{1/2}} + \dfrac{K_2\mathrm{CN_{ISE}^2}}{2K_0} + \dfrac{3K_2\mathrm{CN_{ISE}^3}}{8K_0^{3/2}}\right\}}{\left\{1 + \dfrac{K_1\mathrm{CN_{ISE}}}{2K_0^{1/2}} + \dfrac{K_2\mathrm{CN_{ISE}^2}}{4K_0} + \dfrac{K_2\mathrm{CN_{ISE}^3}}{8K_0^{3/2}}\right\}}\end{aligned} \tag{13}$$

This error is basically the average number of cyanide ligands held per copper ion and is thus unavailable to be measured by the ISE. As such it allows data measured with different total metal ion concentrations ($\mathrm{M_T}$) to be normalised and plotted together as a function of the ISE reading ($\mathrm{CN_{ISE}}$).

A major question for the copper cyanide system is the nature of the $\mathrm{Cu^+}$ term. At high pH, where most ISE cyanide measurements are made, $\mathrm{Cu^+}$ would be expected to form hydroxides. Gupta et al. [8] have pointed out that for zinc, cadmium, and copper the hydroxide forms of the metal should be accounted for in this type of calculation. However, while they showed that this approach worked well for zinc and cadmium, they did not extend it to copper because of a lack of information on the nature of copper(I) hydroxides.

A further problem is that this approach does not account for the effects of mass transport that are important in the functioning of the cyanide ISE. The ISE responds to the concentrations at the electrode surface that depend on the concentration gradients set up between the surface of the AgI and the bulk solution. Therefore, the relative diffusion coefficients of the various species also play a role. The solution for the steady-state fluxes at the electrode for measurement of non-complexed cyanide has been described by Evans [9]. The slightly more complicated case involving equilibrium with a simple complex (such as HCN) has also been shown by Koryta and Stulik [10]. The copper cyanide system is significantly more complicated.

A third problem found was that experimental data showed ISE responses that are consistent with negative numbers of ligands per copper (negative $\varepsilon$ values). This cannot be explained simply by copper cyanide complex equilibria and indicates that other reactions have to be considered.

## 2. Experimental

Standardised 1000 ppm cyanide solution was obtained from Labchem Inc. and standardised 1.0 M NaOH was obtained from VWR. An Orion 9606 combination cyanide selective electrode was used. Samples and standards were made up in NaOH solution of various concentrations (0.1, 0.5 and 1 M). To provide uniform mass transport, the electrode was inserted in the same position into identical glass vial and stir bar sets containing 6.1 ml of sample, and the sample agitated throughout the measurement with a magnetic stirrer set at a controlled stir rate. The electrode was calibrated before and after each set of copper cyanide samples.

## 3. Results and discussion

For a series of prepared solutions with different cyanide to copper ratios, the percent error of the ISE is plotted versus the known total cyanide in Fig. 1. The systematic errors in these readings follow the same general trend, with the ISE under-reading the cyanide at high cyanide concentrations and over-reading at low cyanide concentrations. In Fig. 2, the error per copper

($\varepsilon$, as defined in Eq. (13)) is plotted versus the ISE reading ($CN_{ISE}$) with three different matrix hydroxide concentrations. It can be seen that when the systematic error is plotted per copper ion, the results appear to support cyanide being held by the copper ions at high cyanide concentration (hence an under-reading), and an apparent excess of cyanide (a negative number of cyanide ligands per copper) at low cyanide concentration (an over-reading). The curves also show a shift with pH.

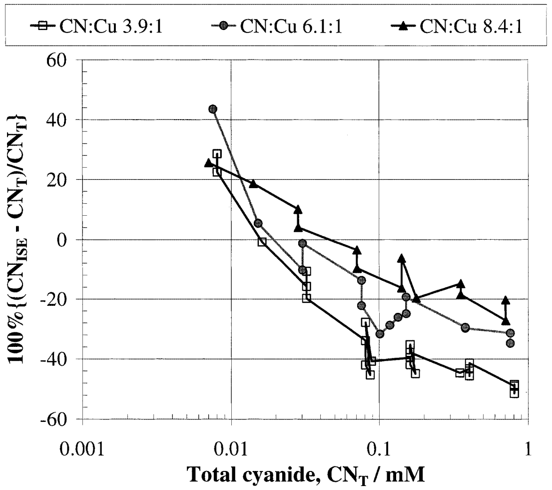

Fig. 1. Percent error in the ISE over its measurement range for three different cyanide to metal ratios in 0.5 M NaOH.

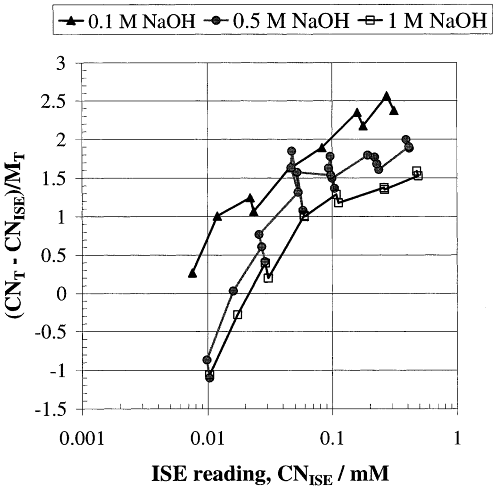

Fig. 2. Error of the ISE measurement ($\varepsilon$) of total cyanide on a per copper basis $(CN_T - CN_{ISE})/M_T$, measured at different hydroxide concentrations (cyanide to copper ratio of 3.9:1).

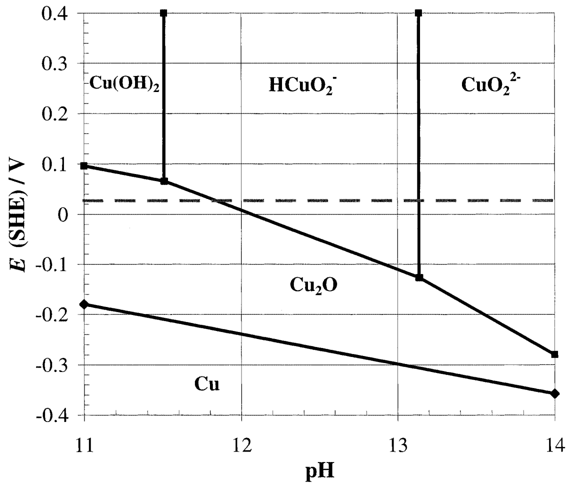

Fig. 3. A Pourbaix type plot showing the stable forms of copper in water for the pH range of interest. A dotted line is also shown for the redox potential for silver/silver iodide in equilibrium with 1 mM iodide.

To predict the response of the ISE at high pH (where most measurements are made to avoid HCN), the chemistry of the metal hydroxides of $Cu^+$ has to be taken into account. As was mentioned in Section 1, this was previously suggested by Gupta et al. [8], but it was not used for copper because of a lack of information on copper(I) hydroxides. According to the Pourbaix Atlas [11], in the pH regions typically used for the ISE measurements, the stable forms of copper are $Cu_2O_{(s)}$, $HCuO_2^-$ and $CuO_2^{2-}$ (see Fig. 3). However, mention is also made of CuOH, which typically converts rapidly to $Cu_2O_{(s)}$. While both of these species are listed as solids, a soluble copper(I) species has been reported experimentally in work done using a copper rotating ring disk electrode in 1 M NaOH by Miller [12]. A further complication is that $HCuO_2^-$ and $CuO_2^{2-}$ are copper(II) species, which would imply an oxidation reaction. If this were true, it might follow that the system would be sensitive to dissolved oxygen or other possible redox species in solution.

On consideration, it was noted that redox reactions of copper(I) with silver(I) could account for the observed measurement of excess cyanide found under some conditions. A line is indicated in Fig. 3 showing the redox potential for the reduction of silver iodide in equilibrium with a solution iodide concentration of $1 \times 10^{-3}$ M. These possible reactions with copper(I) are listed below:

$$Cu^+ + AgI_{(s)} + 3OH^- \rightleftarrows Ag_{(s)} + I^- + HCuO_2^- + H_2O \quad K_4 \qquad (14)$$

$$Cu^+ + AgI_{(s)} + 4OH^- \rightleftarrows Ag_{(s)} + I^- + CuO_2^{2-} + 2H_2O \quad K_5 \qquad (15)$$

These reactions, by releasing $I^-$, could be the cause of the observed over-reading of cyanide by the ISE ($\varepsilon < 0$ in Fig. 2). These reactions would also be favoured at higher hydroxide concentrations, in agreement with the shift to more negative $\varepsilon$ values with higher NaOH concentration in Fig. 2.

For the copper(I), if only soluble species are considered, the reactions of interest might be:

$$Cu^+ + OH^- \rightleftarrows CuOH \quad K_6 \tag{16}$$

$$Cu^+ + 2OH^- \rightleftarrows CuO^- + H_2O \quad K_7 \tag{17}$$

However, no data are available for either of these reactions. The energies of formation of these two species can only be bracketed knowing that their formation from $Cu^+$ and hydroxide would be spontaneous, and so too would be their decomposition into $Cu_2O$. The reaction of copper(I) with iodide to form CuI (which would depress the ISE reading) was also considered, but calculations showed that it would not be significant.

Following the method of Koryta and Stulik [10], one can write expressions for the various fluxes of species to and from the electrode surface (see Fig. 4). The stable species present in the bulk solution (outside the diffusion layer) would be: $CN^-$, $[Cu(CN)_2]^-$, and $[Cu(CN)_3]^{2-}$. The species near the electrode surface (in the region of depleted cyanide) would include the products of the various copper equilibria and the ISE reaction. Assuming steady state (hence no accumulation of any key species at the electrode surface) yields:

*For cyanide:* flux in = flux out

$$\begin{aligned}&([CN^-]_B - [CN^-])D_{CN}\\&+ 3([Cu(CN)_3^{2-}]_B - [Cu(CN)_3^{2-}])D_{Cu(CN)_3^{2-}}\\&+ 2([Cu(CN)_2^-]_B - [Cu(CN)_2^-])D_{Cu(CN)_2^-}\\&= [CuCN]D_{CuCN} + 2[Ag(CN)_2^-]D_{Ag(CN)_2^-}\end{aligned} \tag{18}$$

where the subscript B denotes bulk concentrations, with other concentrations being at the electrode surface, and where $D_i$ is the diffusion coefficient of species 'i'.

*For copper:*

$$\begin{aligned}&([Cu(CN)_3^{2-}]_B - [Cu(CN)_3^{2-}])D_{Cu(CN)_3^{2-}}\\&+ ([Cu(CN)_2^-]_B - [Cu(CN)_2^-])D_{Cu(CN)_2^-}\\&= [CuCN]D_{CuCN} + [Cu^+]D_{Cu^+} + [CuOH]D_{CuOH}\\&\quad + [CuO^-]D_{CuO^-} + [HCuO_2^-]D_{HCuO_2^-}\\&\quad + [CuO_2^{2-}]D_{CuO_2^{2-}}\end{aligned} \tag{19}$$

which can be expanded using the equilibrium constants to give:

$$\begin{aligned}&[Cu(CN)_3^{2-}]_B D_{Cu(CN)_3^{2-}} + [Cu(CN)_2^-]_B D_{Cu(CN)_2^-}\\&= [Cu^+]\Big\{K_3[CN^-]^3 D_{Cu(CN)_3^{2-}} + K_2[CN^-]^2 D_{Cu(CN)_2^-}\\&\quad + K_1[CN^-]D_{CuCN} + D_{Cu^+} + K_6[OH^-]D_{CuOH}\\&\quad + K_7[OH^-]^2 D_{CuO^-} + \frac{K_4[OH^-]^3}{[I^-]}D_{HCuO_2^-}\\&\quad + \frac{K_5[OH^-]^4}{[I^-]}D_{CuO_2^{2-}}\Big\}\end{aligned} \tag{20}$$

And from the stoichiometry of reactions involving iodide (Eqs. (1), (14) and (15)):

$$\begin{aligned}&[Ag(CN)_2^-]D_{Ag(CN)_2^-} + [HCuO_2^-]D_{HCuO_2^-}\\&+ [CuO_2^{2-}]D_{CuO_2^{2-}} = [I^-]D_{I^-}\end{aligned} \tag{21}$$

which can be expanded using the equilibrium constants to give:

$$\begin{aligned}[Ag(CN)_2^-]D_{Ag(CN)_2^-} &= [I^-]D_{I^-}\\&\quad - \frac{K_4[Cu^+][OH^-]^3}{[I^-]}D_{HCuO_2^-}\\&\quad - \frac{K_5[Cu^+][OH^-]^4}{[I^-]}D_{CuO_2^{2-}}\end{aligned} \tag{22}$$

Substituting Eqs. (20) and (22) into Eq. (18) to eliminate $[Ag(CN)_2^-]$ and $[Cu^+]$ gives

$$\begin{aligned}&[CN^-]_B D_{CN^-} + 3[Cu(CN)_3^{2-}]_B D_{Cu(CN)_3^{2-}}\\&\quad + 2[Cu(CN)_2^-]_B D_{Cu(CN)_2^-}\\&\quad = 2[I^-]D_{I^-} + [CN^-]D_{CN^-} + \{Cu(CN)_3^{2-}]_B D_{Cu(CN)_3^{2-}}\\&\qquad + [Cu(CN)_2^-]_B D_{Cu(CN)_2^-}\}S\end{aligned} \tag{23}$$

where the term $S$ is the number of cyanide ligands associated with the dominant copper species at the electrode surface:

$$S = \left\{\frac{3K_3[CN^-]^3 D_{Cu(CN)_3^{2-}} + 2K_2[CN^-]^2 D_{Cu(CN)_2^-} + K_1[CN^-]D_{CuCN} - 2\frac{K_4[OH^-]^3}{[I^-]}D_{HCuO_2^-} - 2\frac{K_5[OH^-]^4}{[I^-]}D_{CuO_2^{2-}}}{K_3[CN^-]^3 D_{Cu(CN)_3^{2-}} + K_2[CN^-]^2 D_{Cu(CN)_2^-} + K_1[CN^-]D_{CuCN} + D_{Cu^+} + K_6[OH^-]D_{CuOH} + K_7[OH^-]^2 D_{CuO^-} + \frac{K_4[OH^-]^3}{[I^-]}D_{HCuO_2^-} + \frac{K_5[OH^-]^4}{[I^-]}D_{CuO_2^{2-}}}\right\} \tag{24}$$

This result is far more complicated than the equations developed previously and must be solved by itera-

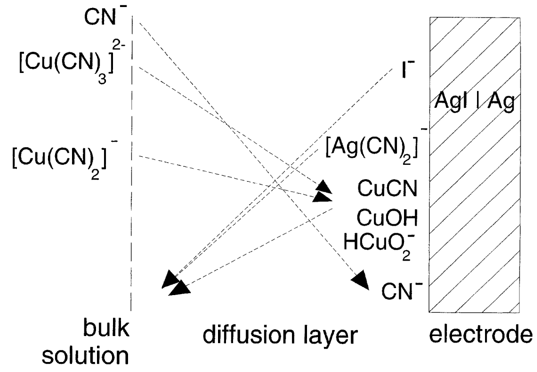

Fig. 4. Important species fluxes at the cyanide ISE electrode.

tion. This involves setting up a second equation using the ISE equilibrium, Eq. (1), to eliminate $[Ag(CN)_2]^-$ from Eq. (22), then using this to eliminate $[Cu^+]$ from Eq. (20). For unknown solutions, the bulk total cyanide value would have to be guessed, then the bulk species concentrations calculated using the copper concentration ($M_T$). Using these estimated values for the bulk concentrations of $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_2]^-$, this second equation can be solved iteratively for the surface free cyanide concentration. This value can be used in Eq. (23) to improve the bulk total cyanide estimation. Also, it should be noted that when mass transfer is considered, rather than using Eq. (8), the equation for relating the calibrated ISE reading (i.e. without metal ions present) to the iodide concentration is given by:

$$CN_{ISE} = 2[I^-]\frac{D_{I^-}}{D_{CN^-}} \quad \text{(see Refs. [9,10])} \tag{25}$$

For the known bulk solutions in this work, the known bulk concentrations of $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_2]^-$ were used along with known $M_T$ and $CN_{ISE}$ values, and the system was solved iteratively for the estimated surface cyanide concentration ($[CN^-]$). This was used with Eq. (23) to give predicted $\varepsilon$ values, which could be compared to the experimental values to test the validity of these equations. It was found that this approach could predict the correct general trends in $\varepsilon$ values observed in the data (using the formation energies of CuOH and $CuO^-$ as adjustable parameters). However, the best fits were obtained using hydroxide concentrations smaller than the actual values and the model would not predict $\varepsilon$ values below $-0.5$. Some uncertainties arise because many of the constants are not precisely known and some are unknown. Another consideration is that some reactions might be kinetically limited. If the correct hydroxide values are used in the model, the predictions show that the copper(II) hydroxide species dominate, leading to $\varepsilon$ values of between 0.5 and $-0.5$. If the copper(II) hydroxide formation reactions were considered to be kinetically limited, a better fit would be obtained. Also, the approach used in developing the equations does not include the possibility of reactions between the various components within the diffusion layer (this would require finite element analysis). One of the more interesting possible reactions would be the interaction of outward diffusing copper(II) species with inward diffusing cyanide which would be expected to result in the oxidation of some of the cyanide [14]. For example:

$$2HCuO_2^- + CN^- + H_2O = CNO^- + 2CuOH + 2OH^- \tag{26}$$

While this results in a decrease of cyanide at the electrode surface, because of the formation of new copper(I) species, it would result in a net higher cyanide reading because of the reactions of copper(I) with silver iodide (Eqs. (14) and (15)). This may explain some of the very negative $\varepsilon$ values observed. A final concern is related to the actual experimental $\varepsilon$ values. Because the $\varepsilon$ values are obtained by the difference between two larger values ($CN_T - CN_{ISE}$) this can lead to significant error especially at higher cyanide to metal ratios (for Fig. 2, the data for the lowest measured cyanide to copper ratio of 3.9:1 are shown). Thus, because of these uncertainties and because of concerns about ease of use, further refinement of the model does not seem justified.

Consequently, it is perhaps more useful to investigate the implications of these results and use them to develop a semi-empirical approach. To use the fundamentally derived equation in a semi-empirical manner, one must first put it in a more usable form. This was done by substituting Eq. (25) into Eqs. (23) and (24) to replace $[I^-]$ with $CN_{ISE}$, and also adding in the bulk total cyanide term:

$$CN_T = [CN^-]_B + 3[Cu(CN)_3^{2-}]_B + 2[Cu(CN)_2^-]_B \tag{27}$$

This results in:

$$\begin{aligned} CN_T = CN_{ISE} + [CN^-] \\ + [Cu(CN)_3^{2-}]_B\left\{3 - \frac{D_{Cu(CN)_3^{2-}}}{D_{CN^-}}(3 - S)\right\} \\ + [Cu(CN)_2^-]_B\left\{2 - \frac{D_{Cu(CN)_2^-}}{D_{CN^-}}(2 - S)\right\} \end{aligned} \tag{28}$$

Noting that the equilibrium constant of Eq. (1) is large, one can assume that $CN_{ISE} \gg [CN^-]$ (as was done in Section 1 using Eqs. (8) and (12)). Then for the case where the main bulk copper species is $[Cu(CN)_3]^{2-}$, Eq. (28) can be reformulated in terms of $\varepsilon$ (like Eq. (13)) to give:

$$\varepsilon = 3 - \frac{D_{Cu(CN)_3^{2-}}}{D_{CN^-}}(3 - S) \tag{29}$$

Similarly, if the main bulk copper species is $[Cu(CN)_2]^-$, the corresponding equation is:

$$\varepsilon = 2 - \frac{D_{Cu(CN)_2^-}}{D_{CN^-}}(2 - S) \tag{30}$$

Equilibrium calculations for the bulk concentrations have shown that at free cyanide concentrations near the upper range of the ISE, the copper will be mainly $[Cu(CN)_3]^{2-}$ while at the low end of the range $[Cu(CN)_2]^-$ begins to dominate. (The two species will be of equal concentration when the free cyanide concentration is around 0.026 mM.) Thus, one can predict $\varepsilon$ values for the high and low ends of the ISE range for each possible species dominant at the electrode surface. This is shown in Table 1, where for an assumed dominant species at the electrode surface a value of $S$ (Eq. (24)) can be calculated. This can then be used in either Eq. (29) or (30) to calculate the error factor ($\varepsilon$), depend-

Table 1
Expected error factors ($\varepsilon$) as a function of the dominant bulk solution species and electrode surface species

| Dominant surface species | $S$ | Dominant bulk species | |
|---|---|---|---|
| | | $[Cu(CN)_3]^{2-}$ | $[Cu(CN)_2]^-$ |
| $[Cu(CN)_3]^{2-}$ | 3 | 3 | |
| $[Cu(CN)_2]^-$ | 2 | 2.48 | 2 |
| CuCN | 1 | 1.96 | 1.31 |
| $Cu^+$, CuOH, $CuO^-$ | 0 | 1.44 | 0.62 |
| $HCuO_2^-$, $CuO_2^{2-}$ | −2 | 0.40 | −0.75 |

$D_{CN^-} = 2.08 \times 10^{-5}$ cm$^{-2}$ s$^{-1}$ [6], $D[Cu(CN)_3]^{2-} = 1.08 \times 10^{-5}$ cm$^{-2}$ s$^{-1}$ [13] and $D_{[Cu(CN)_2]^-} = 1.43 \times 10^{-5}$ cm$^{-2}$ s$^{-1}$ [13] are used.

ing on which species is assumed to be dominant in the bulk solution.

One can then take Eq. (28) and simplify it to a form similar to Eq. (11) by including terms for only a few key species which dominate the response of the ISE. These key species can be included, using their effect on the cyanide measurement (the $\varepsilon$ values from Table 1), and using a functional relationship with respect to the ISE reading ($CN_{ISE}$) developed in Eq. (24). This latter uses Eq. (25) and also involves making the simplifying approximation that the ISE reading is roughly related to the amount of free cyanide (i.e. assuming as an approximation that the effect of reactions (14) and (15) is not large over most of the ISE's range). Note that the effect of reactions (14) and (15) is still included in the semi-empirical equation through the choice of key species. The key species influencing the response of the ISE at different cyanide and hydroxide concentrations can be determined by comparing the calculated $\varepsilon$ values in Table 1 with the experimentally obtained values in Fig. 2.

For the data in 0.1 M NaOH, at the high end of the cyanide range (where $[Cu(CN)_3]^{2-}$ is the dominant bulk species), $\varepsilon$ equals 2.5 implying that $[Cu(CN)_2]^-$ is the dominant species at the electrode surface. The mid range $\varepsilon$ values are between 2 and 1 implying CuCN and copper(I) hydroxide species dominate, and at low cyanide values (where $[Cu(CN)_2]^-$ would be the dominant bulk solution copper species) $\varepsilon$ equals 0 indicating a mix of copper(I) and copper(II) oxide or hydroxide species.

Thus, one can then write a semi-empirical equation using the $\varepsilon$ values and the expected relationships with the ISE reading for the various dominant species:

$$CN_T = CN_{ISE} + M_T \left\{ \frac{2.48\alpha_1 CN_{ISE}^2 + 1.96\alpha_2 CN_{ISE} + 1.0\alpha_3 - \dfrac{0.75}{CN_{ISE}}}{\alpha_1 CN_{ISE}^2 + \alpha_2 CN_{ISE} + \alpha_3 + \dfrac{1}{CN_{ISE}}} \right\} \tag{31}$$

where $\alpha_1$, $\alpha_2$, and $\alpha_3$ are determined experimentally and the 1.0 term comes from averaging the 1.44 and 0.62 terms for copper(I) hydroxides in Table 1. Moreover a good fit can still be obtained with only two experimentally determined factors. Therefore, a further simplified form was created with an approximate term created to represent all the copper(I) species:

$$CN_T = CN_{ISE} + M_T \left\{ \frac{2.5\alpha_1 CN_{ISE}^2 + 1.5\alpha_2 CN_{ISE}^{0.5} - \dfrac{0.75}{CN_{ISE}}}{\alpha_1 CN_{ISE}^2 + \alpha_2 CN_{ISE}^{0.5} + \dfrac{1}{CN_{ISE}}} \right\} \tag{32}$$

In this equation, the $\alpha_1$ value is approximately related to the formation constant of the species represented by the first term (i.e. $[Cu(CN)_2]^-$) divided by the formation constant for the species represented by the third term (the copper(II) oxides). Similarly, the $\alpha_2$ value is approximately related to the formation constant of the copper(I) species represented by the second term divided by the formation constant for the copper(II) oxide species represented by the third term. Thus, adjusting these terms shifts the regions of stability of the dominant species as predicted by this equation. This approach was also extended to higher matrix pHs which, based on the discussion of the various copper reactions, should favour the copper oxide species.

The data measured in 0.5 M NaOH differs in that the $\varepsilon$ value at high cyanide levels (where $[Cu(CN)_3]^{2-}$ is the dominant bulk solution species) is around 2. This implies that at higher hydroxide levels $[Cu(CN)_2]^-$ does not play a significant role at the electrode surface. It was also found that at the low cyanide end of the ISE range the $\varepsilon$ value is around $-1$, lower than can be explained by the model. As was discussed earlier, this could be due to reactions between the copper(II) species and cyanide in the diffusion layer. Thus, the equation for estimating total cyanide at 0.5 M NaOH is:

$$CN_T = CN_{ISE} + M_T \left\{ \frac{1.96\alpha_1 CN_{ISE} + 1.0\alpha_2 - \dfrac{1.5}{CN_{ISE}}}{\alpha_1 CN_{ISE} + \alpha_2 + \dfrac{1}{CN_{ISE}}} \right\} \tag{33}$$

At 1 M NaOH, the $\varepsilon$ value at high cyanide levels is around 1.5 indicating that the dominant surface species are copper(I) hydroxides. In the middle of the ISE range, the $\varepsilon$ value around 0.4 corresponds to copper(II) hydroxides (with the main bulk solution copper species being $[Cu(CN)_3]^{2-}$). The $\varepsilon$ value at the low end of the ISE range is then determined by copper(II) hydroxides formed from $[Cu(CN)_2]^-$ bulk solution species. While in the other cases, the shift of the bulk solution species could be included in the change of the dominant elec-

Table 2
Values obtained in this work for fitting of data (shown in Fig. 5)

| Electrolyte | $\alpha_1$ | $\alpha_2$ | Standard error of estimation of $\varepsilon$ [a] |
|---|---|---|---|
| 0.1 M NaOH (Eq. (32)) | $3.1\times10^4$ mM$^{-3}$ | $7.4\times10^2$ mM$^{-1.5}$ | 0.23 |
| 0.5 M NaOH (Eq. (33)) | $1.6\times10^3$ mM$^{-2}$ | $2.1\times10$ mM$^{-1}$ | 0.28 |
| 1 M NaOH (Eq. (34)) | $1.8\times10^3$ mM$^{-2}$ | 7.6 mM$^{-1}$ | 0.16 |

[a] Given by $s_{y,x} = [\Sigma(y_i - y_{i,est.})^2/(N-2)]^{1/2}$, where the $y_i$ are experimentally determined values, the $y_{i,est.}$ are calculated values, and $N$ is the number of data points.

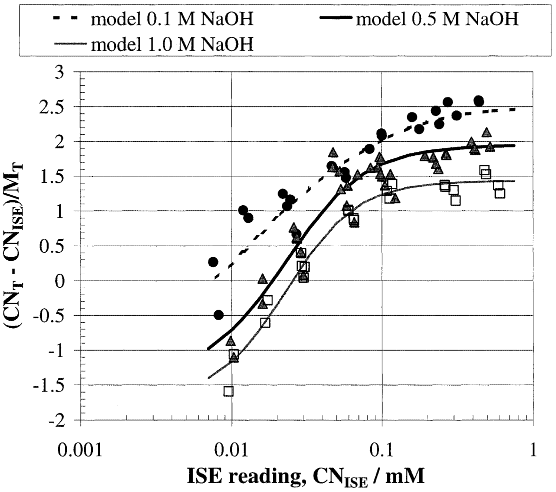

Fig. 5. Experimental data with curves fitted using the expressions given in the text for the particular matrix pH, with parameters from Table 2. Combined data for 3.9:1 and 6.1:1 cyanide to copper ratios are shown measured in 0.1 (circle), 0.5 (triangle) and 1.0 M NaOH (square).

trode surface species, this is not possible for the 1 M NaOH case. If however, it is assumed that the fraction of the bulk copper concentration which is $[\mathrm{Cu(CN)_2}]^-$ increases with decreasing cyanide, a $1/\mathrm{CN}_{\mathrm{ISE}}^2$ term can be used to represent the changing dominant bulk species and an approximate form of the equation would be:

$$\mathrm{CN_T} = \mathrm{CN_{ISE}} + \mathrm{M_T}\left\{\frac{1.44\alpha_1 + \dfrac{0.4\alpha_2}{\mathrm{CN_{ISE}}} - \dfrac{1.5}{\mathrm{CN_{ISE}^2}}}{\alpha_1 + \dfrac{\alpha_2}{\mathrm{CN_{ISE}}} + \dfrac{1}{\mathrm{CN_{ISE}^2}}}\right\} \qquad (34)$$

The fits obtained with these equations for the different test matrices are shown in Fig. 5 with the values of the adjustable parameters found in this work listed in Table 2. These adjustable parameter values were obtained by minimising the sum of the squares of the residual errors in the estimate of $\varepsilon$, as calculated using an Excel spreadsheet. As might be expected from the discussion of the nature of the $\alpha_i$ terms, they control the regions of stability of the various dominant species. When fitting the experimental data, the $\alpha_1$ term adjusts the point where the first term in the equation ceases to dominate, and the $\varepsilon$ value begins to drop as the ISE reading ($\mathrm{CN_{ISE}}$) decreases. The $\alpha_2$ term adjusts the relative stability of the second versus the third term in the equation and thus affects the middle of the fitted curve, controlling the rate at which the $\varepsilon$ value decreases to the final third term (lowest $\varepsilon$) value.

## 4. Conclusions

The response of the cyanide ISE in the presence of copper is quite complex. This complexity arises from the mass transfer controlled nature of the cyanide ISE response, the copper cyanide equilibria, and possibly from direct interactions of copper ions with the silver iodide electrode. It has also been found that these equilibria are affected by the pH of the matrix used for the measurements.

Because of the complex nature of the system, a semi-empirical calibration appears to be the best approach for using the ISE under these conditions. Using this approach, a calculated 'error factor' can be used to estimate the total cyanide concentration from the ISE reading and the copper concentration. This provides a rapid and convenient method for measuring total cyanide in copper metal containing solutions.

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## References

[1] Orion Instruction Manual for the 9406/9606 Cyanide Electrode, Orion Research Inc., Beverly, MA, 1997.

[2] Total and Amenable Cyanide: Distillation, US Environmental Protection Agency, EPA Method 9010B.

[3] Potentiometric Determination of Cyanide in Aqueous Samples and Distillates with Ion-Selective Electrodes, US Environmental Protection Agency, EPA Method 9213.

[4] R.D. Rocklin, E.L. Johnson, Anal. Chem. 55 (1983) 4.
[5] M. Mascini, A. Napoli, Anal. Chem. 46 (1974) 447.
[6] D.R. Lide, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1999.
[7] J.A. Dean, Lange's Handbook of Chemistry, McGraw-Hill, New York, 1999.
[8] A. Gupta, E.F. Johnson, R.H. Schlossel, Anal. Chim. Acta 171 (1985) 351.
[9] D.H. Evans, Anal. Chem. 44 (1972) 875.
[10] J. Koryta, K. Stulik, Ion Selective Electrodes, Cambridge University Press, Cambridge, UK, 1983 (p. 50).
[11] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed., NACE, Houston, 1974.
[12] B. Miller, J. Electrochem. Soc. 116 (1969) 1675.
[13] D.A. Dudek, P.S. Fedkiw, J. Electroanal. Chem. 474 (1999) 16.
[14] J.K. Beattie, G.A. Polyblank, Aust. J. Chem. 48 (1995) 861.