

# ONLINE CYANIDE MEASUREMENT AND CONTROL FOR COMPLEX ORES

By

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## 1. INTRODUCTION

The gold industry in the past couple of decades has looked to implement better control of cyanide addition to the leach circuit in order to optimise cyanide usage, subsequent cyanide destruction costs and the environmental risks. The implementation of online cyanide measurement as a feedback control parameter has proven problematic in several cases. The issues can be categorised as:

Analyser reliability/acceptance which includes:

- limited output,
- filtration issues,
- maintenance, and
- differences between laboratory and analyser readings.

Solution complexity/interferences such as:

- sulphides,
- metal cyanides, and
- pH.

Control strategy/parameters:

- cyanide measurement variability,
- tank residence time, and
- cyanide demand.

With the gold industry looking to process more complex ores, the control of cyanide addition to the gold leaching circuit has become more crucial. On-line cyanide measurement provides a rapid response to changes in ore mineralogy, however poor understanding of the methods and/or reliability issues described above have impaired their uptake within the gold industry. This paper discusses the potentiometric end-point silver nitrate titration method, the most common on-line analysis technique adopted for “free” cyanide, and its comparison to the common site laboratory rhodanine endpoint silver nitrate titration method. In particular the influence of metal cyanides and the effect of titration pH on the “free” cyanide measurement using these two methods are presented and discussed. At some operations, the presence of clay minerals and/or fine particle size (e.g. fine grinding used in order to expose the gold), results in difficulties in maintaining filtered solution to the analyser.

Examples of these issues are presented and discussed in this paper along with some findings and knowledge gained from investigations into many of these issues. Some solutions are proposed whilst areas needing further investigation are highlighted.

## 2. CYANIDE MEASUREMENT

Methods commonly used to measure cyanide concentration determine either:

- free (titratable) cyanide,
- weak acid dissociable (WAD) cyanide, or
- total cyanide.

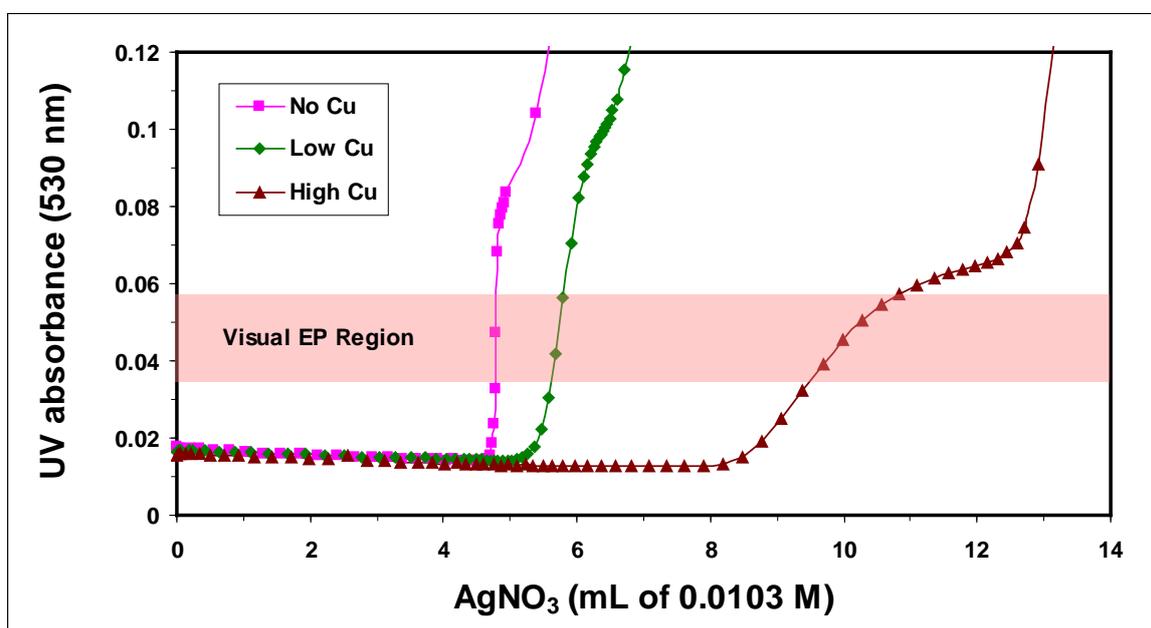
The cyanide concentration of interest in the leaching of gold is the cyanide available in solution which can leach gold. The free cyanide methods measure the free and very weakly complexed (such as the fourth cyanide complexed with copper) cyanide ions and thus provides a cyanide determination that best reflects the available cyanide for gold leaching; some weak acid dissociable cyanide ions, such as the third cyanide complexed with copper, are also available to leach gold, though the gold leach rate is much lower than for free cyanide (Breuer et al., 2005). However, the free cyanide measurement can be misleading in the treatment of more complex ores where achieving a leach pH above 9.5 is uneconomical or copper is present in solution (Breuer and

Rumball, 2007). The most commonly used methods for determining the free cyanide involve titration with silver nitrate using either rhodanine indicator or the potential of a silver wire to ascertain the endpoint.

To interpret the free cyanide titration results it is vital to know the solution species present and the influence these may have on the free cyanide determination. This not only includes the metal cyanides, but also other anions in solution which can complex with silver (for example sulfide and thiosulfate). Traditional analyses for elements such as AAS and ICP can quantify the metal ions, but techniques such as HPLC are required to provide information on the various anion species (Breuer et al., 2009).

## 2.1. SILVER NITRATE TITRATION WITH RHODANINE ENDPOINT DETECTION

For simple solutions the colour change of the rhodanine indicator is quite sharp. This is shown in Figure 1 where a sharp increase in UV absorbance of the titration solutions occurs at the endpoint for a solution containing only sodium cyanide. Also shown is the much slower colour change observed when copper is present, which makes identifying the endpoint more difficult and as such interpreting the end-point can produce significant variation in results by different operators.



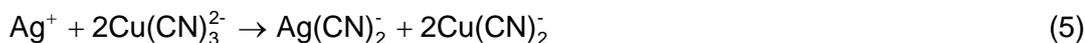
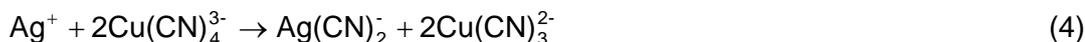
**Figure 1: UV absorbance of rhodanine indicator during titration of 250 mg/L NaCN solution with silver nitrate; low Cu – 115 mg/L Cu as  $\text{Cu}(\text{CN})_3^{2-}$ , high Cu – 530 mg/L Cu as  $\text{Cu}(\text{CN})_3^{2-}$ .**

As a solution containing cyanide is titrated with silver nitrate, the added silver ions complex the free cyanide ions (Equation 1). The silver ions form a more stable complex with cyanide than rhodanine and thus a colour change from silver complexing with the rhodanine (Equation 2) does not occur until all the free cyanide has been complexed with silver. Further addition of silver nitrate then results in precipitation of silver cyanide (Equation 3).



With copper present in the cyanide solution the titration becomes more complex as the cyanide associated with the copper can also be released and be complexed with silver ions. The fourth cyanide complexed with copper is weak and thus is titrated (Equation 4) along with the free cyanide

(see potentiometric endpoint determinations below). The cyanide ions complexed with copper tri-cyanide can also complex with silver ions (Equation 5), which according to Figure 1 is a competing reaction with rhodanine (Equation 2). Hence, the rhodanine colour change becomes broader and the endpoint more difficult to identify as the copper concentration increases.



## 2.2. SILVER NITRATE TITRATION WITH POTENTIOMETRIC ENDPOINT DETECTION

A potentiometric endpoint determination uses the measured potential of a silver wire in the titration solution as an indicator of changes in solution speciation as silver nitrate is added. The change in the potential of a silver wire during the silver nitrate titration of cyanide solutions in the absence and presence of copper is shown in Figure 2. For the solution without copper, a sharp change in the measured potential of the silver wire, and hence a maximum in the potential change, occurs when all the cyanide has been complexed with silver ions. Notably, in the presence of copper the endpoint is not changed (cf. Figure 1 for rhodanine), though the potential change is less sharp. This potentiometric endpoint corresponds with the free cyanide ions and the fourth cyanide associated with copper (i.e. each copper at the end-point has three cyanide ions remaining complexed with it). Thus, in copper cyanide solutions the rhodanine method will give higher cyanide results than the potentiometric method, with the extent dependent on the copper concentration.

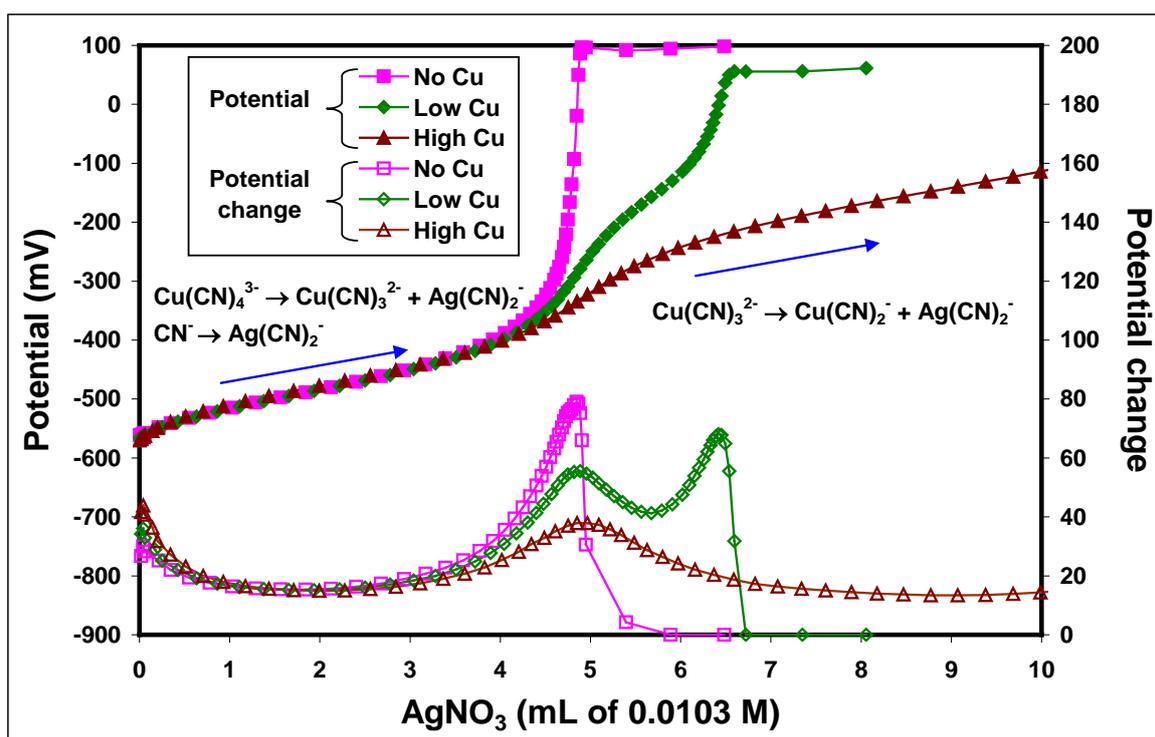
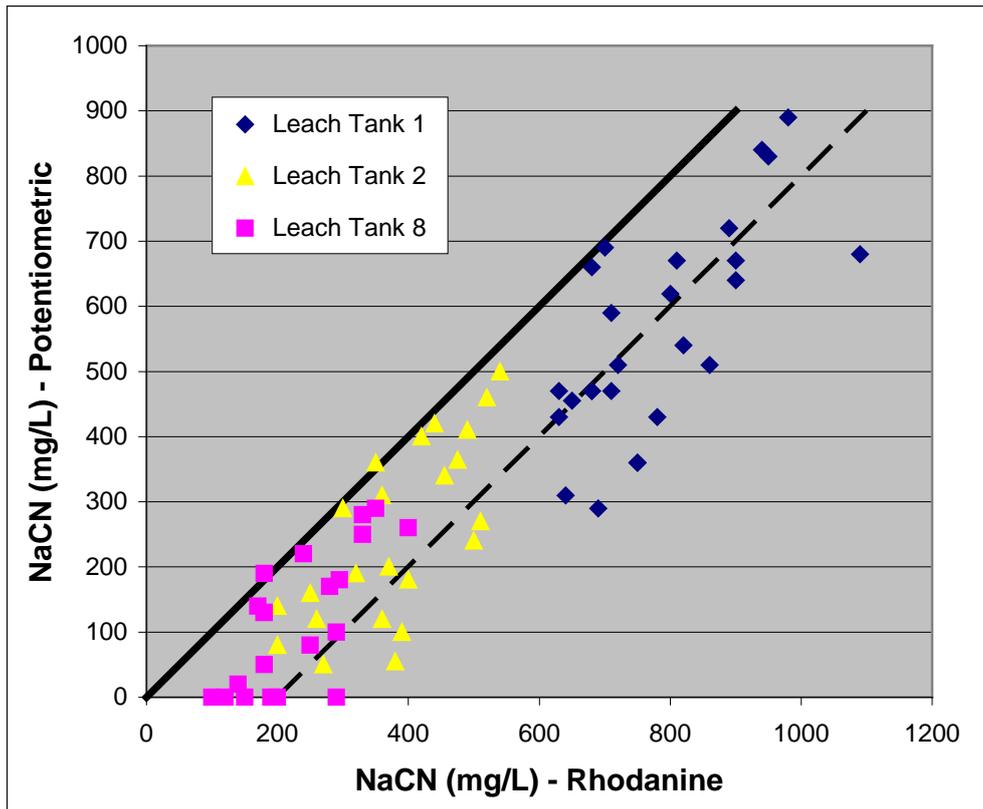


Figure 2: Silver wire potential during silver nitrate titration of the same cyanide solutions as in Figure 1.

Figure 3 shows a comparison of potentiometric (off-site laboratory) and rhodanine (operator) titrations for plant solutions over a 12 month period; copper concentrations in the leach solutions were typically 200 – 500 mg/L. These results are consistent with the effect of copper described above. The rhodanine titration results are around 200 mg/L higher than those determined by potentiometric titration. Further investigations are currently being conducted to establish a correlation between the two cyanide measurements.



**Figure 3: Comparison of potentiometric (off-site laboratory) and rhodanine (operator) titrations for plant solutions over a 12 month period (typically 200-500 mg/L copper).**

### 2.3. OTHER INTERFERENCES TO THE SILVER NITRATE TITRATION

In the extraction of gold from sulfide ores using cyanide, there is the potential for sulfide ions to form in solution at the beginning of the leach. If sulfide ions are present in the cyanide solution, silver sulfide precipitates rapidly upon the first addition of silver nitrate (Equation 6). This masks the rhodanine colour and thus the sulfide ions must first be removed by the addition of lead(II) ions with the pH maintained above 11 (Breuer and Rumball, 2007). The silver sulfide forms preferential to silver cyanide and thus doesn't have to be removed for a potentiometric titration (Figure 4); this also allows quantification of the sulfide ion concentration.



Depending on the pH of the cyanide solution being titrated, both  $\text{CN}^-$  and  $\text{HCN}_{(\text{aq})}$  can be present. The  $\text{CN}^-/\text{HCN}_{(\text{aq})}$  distribution as a function of pH is described by Equation 7 ( $\text{pK}_a = 9.2$ ).  $\text{HCN}_{(\text{aq})}$  is not measured, but is included in the determination if there is sufficient buffer present (Breuer and Rumball, 2007). The addition of NaOH to the titration is used where there is insufficient buffer to remove the influence of pH on the cyanide measurement; low pH and insufficient buffer are indicated by a difference in measured cyanide values with and without the addition of NaOH.

$$\frac{[\text{CN}^-]}{[\text{HCN}_{(\text{aq})}]} = 10^{(\text{pH}-\text{pK}_a)} \quad (7)$$

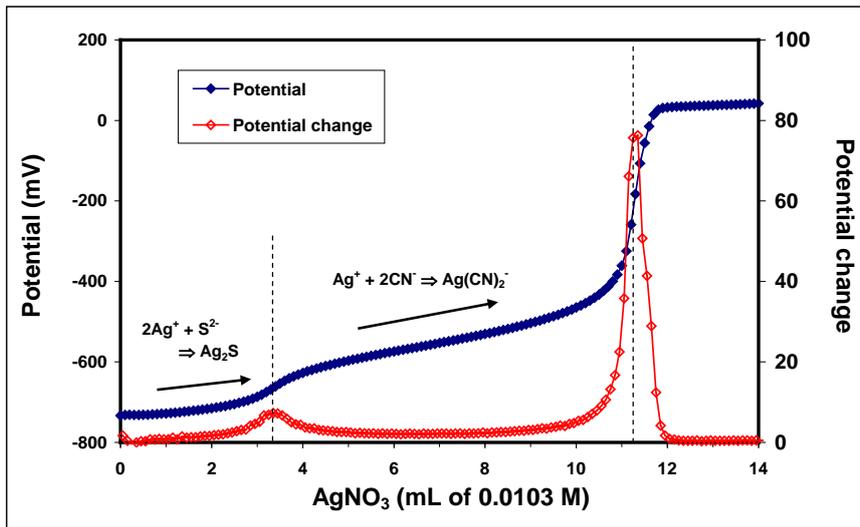


Figure 4: Potentiometric silver nitrate titration of cyanide solution (2 mL, 4000 mg/L NaCN) containing 270 mg/L sulfide ions.

Zinc, if present in the gold ore, may also dissolve during cyanidation being complexed by cyanide ions at pH's less than 12, or hydroxide ions at high pH's. Rhodanine titration of zinc cyanide solutions of various pH values in the range 9 – 13 found that the measured cyanide was independent of pH and equivalent to the total cyanide in solution. This indicates that the cyanide ions complexed with zinc are only weakly bound and are easily released and complex with silver ions in preference to rhodanine. However, for the potentiometric titration, the presence of zinc ions complicates the results if the pH is below 12 (Figure 5). At high pH (NaOH added to the titration) the zinc is complexed with hydroxide ions and thus a single titration endpoint is observed corresponding to the total cyanide. Without NaOH addition (pH = 10.5) the zinc is complexed with cyanide and two additional transitions (maxima in the rate of potential change) are observed at the addition of 2.5 and 3.8 mL of silver nitrate solution. These respectively correspond closely to four and three cyanide ions remaining complexed with the zinc. Depending on solution composition these peaks independently become more or less distinguishable and thus in some cases just a single inflection is observed. Thus, to avoid incorrect or varying automated endpoint identification, the determination is best simplified with the addition of NaOH to the titration. Also, as the cyanide complexed with zinc is only weakly bound (weaker than the third cyanide associated with copper which is known to leach gold), it is most likely available for gold dissolution and thus with the addition of NaOH to the titration provides a cyanide measurement applicable to that available for gold leaching.

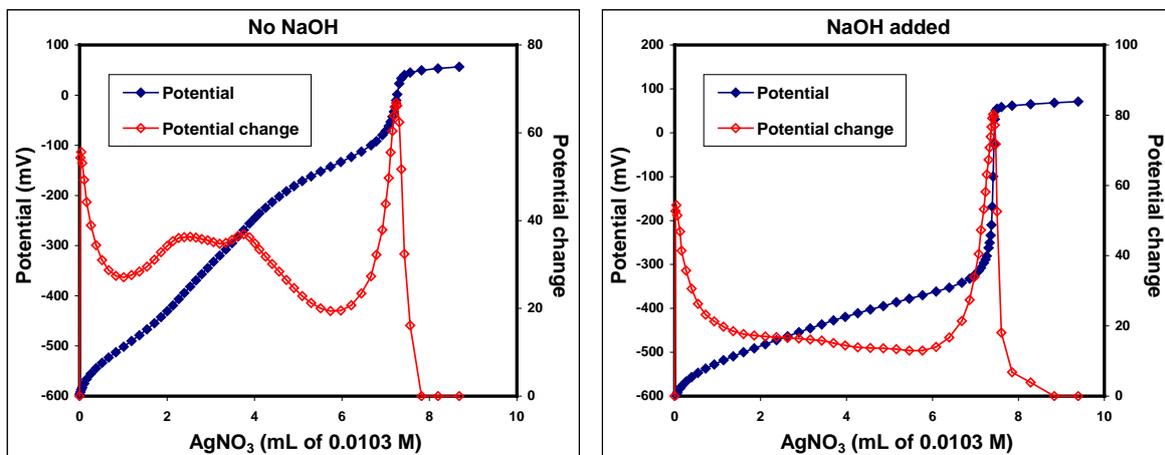
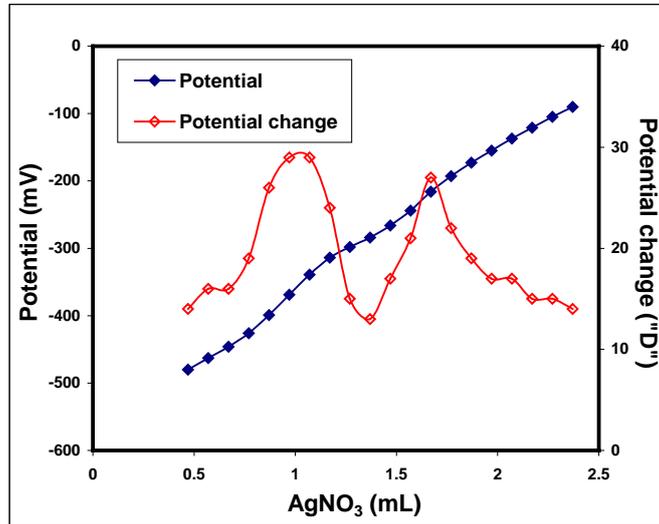


Figure 5: Potentiometric silver nitrate titration of cyanide solution (5 mL, 1500 mg/L NaCN) containing 320 mg/L zinc ions without (left) and with (right) NaOH added.

The effect of dissolved zinc on the online potentiometric cyanide measurement at a gold operation is shown in Figure 6. The Orica OCM5000 cyanide analyser used in this case identified the endpoint within a defined potential window as the largest change in the measured potential of the silver wire in the titration solution. This potentiometric titration curve has low changes in the measured potential (differential) and two peaks in the differential curve are observed within the potential window. The relativity of these two differential peaks was observed to vary between measurements and on occasions the first peak had the higher potential change. This may account for some sharp changes and lower cyanide concentrations determined by the online analyser measurement previously.



**Figure 6: Orica OCM5000 online potentiometric silver nitrate titration of a cyanidation leach solution (12 mL sample, 5.199 g/L silver nitrate).**

Online analysers typically don't store the titration data or display the titration curve for interpretation, and connection to a PC is thus required to obtain this information; hence this information may only be accessible by the vendor. This obviously impedes the troubleshooting of the analyser and has no doubt contributed to the lack of acceptance and implementation at operations.

Manual potentiometric titration curves for the same solution without and with the addition of NaOH are shown in Figure 7. Without the addition of NaOH a similar titration curve is observed to that shown in Figure 6, however only one endpoint is observed with NaOH added to the titration. This single peak with NaOH added corresponds closely with the second peak without NaOH addition. The concentration of zinc in the solution also supported that the first of the two peaks was due to cyanide ions complexed with zinc. In this case the potential window of the online analyser was reduced (starting potential increased) such that the first differential peak observed at around -375 mV was excluded from the endpoint window. An alternative is to retrofit the on-line analyser to add some caustic to the titration (as is done at some operations where the titration pH is raised to avoid unmeasured HCN, the quantity of which is dependent on pH).

The accuracy of the endpoint with 0.1 mL additions used in the online titration is  $\pm 15$  mg/L NaCN for a 10 mL titre; other errors such as variability in titre volumes would add to this. The accuracy of the cyanide measurement may be improved by decreasing the silver nitrate concentration, though limited by the maximum cyanide concentration to be encountered and the titration vessel volume.

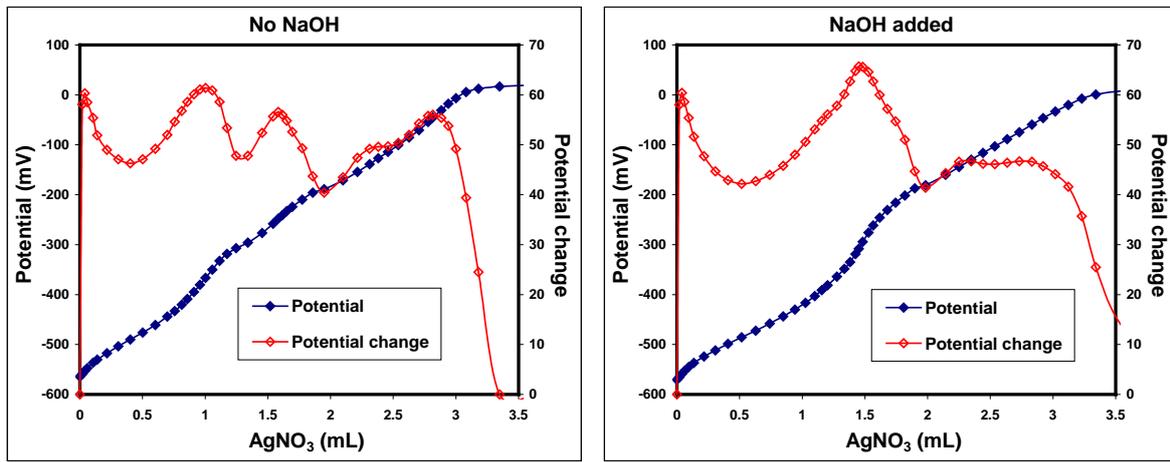


Figure 7: Manual potentiometric titration curves for the same solution analysed in Figure 6 without (left) and with (right) NaOH added (10 mL sample, 5.199 g/L silver nitrate).

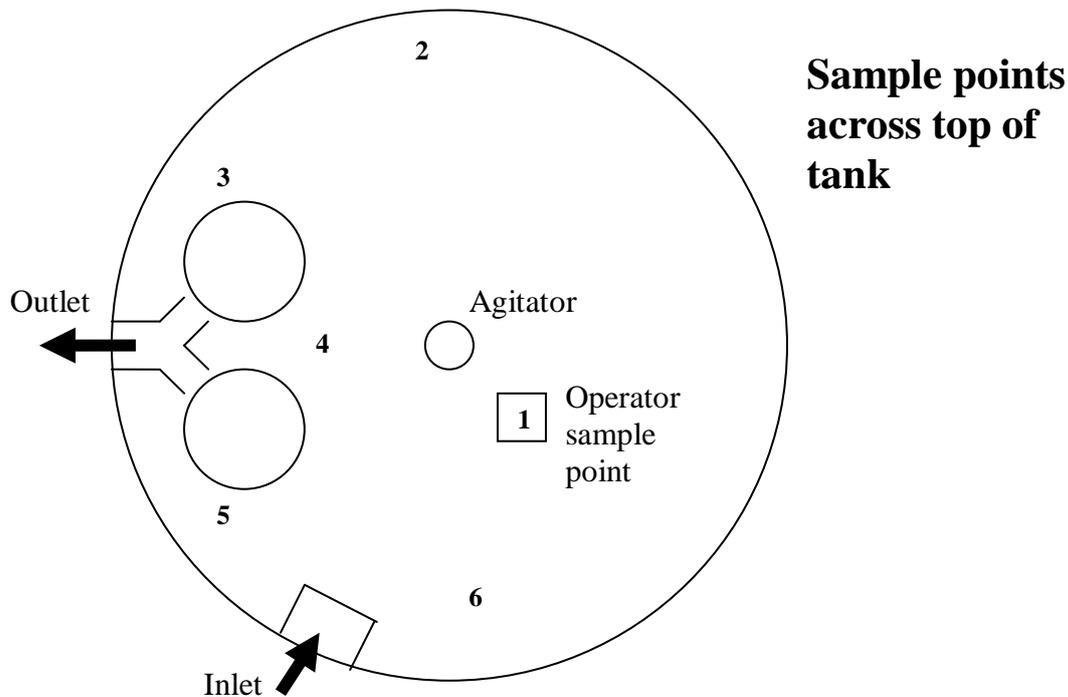
### 3. ONLINE CYANIDE MEASUREMENT

#### 3.1. SAMPLING VARIABILITY

A survey was conducted at a gold operation over the top of the first cyanide leach tank at the points identified in Figure 5. Cyanide is added into this tank in the downcomer with the inlet feed. The variability in the free cyanide measurements by potentiometric titration (Table 1) was 50 mg/L NaCN between the highest and lowest across the points surveyed with a much lower variability of less than 5 mg/L NaCN observed in the majority of the duplicate assays. The observed variability between sample points gives a good indication of the variability expected in the operator and online analyser measurements from the variability within the tank (a similar assessment could also be made by sampling the same point several times at one minute intervals and analysing). If it is assumed operator and analyser variability is around 15 mg/L NaCN then the variability of cyanide measurements will be at best  $\pm 40$  mg/L of the average tank concentration.

Table 1: Cyanide concentrations at the top of the leach tank for the positions shown in Figure 8.

Position	Cyanide (mg/L NaCN)	
	A	B
1	733	732
2	694	693
3	705	706
4	685	685
5	712	709
6	727	717



**Figure 8: Plan view of the location points where samples were taken at the top of the first leach tank.**

### 3.2. ANALYSER PERFORMANCE

The long term successful use of an Orica OCM5000 on-line cyanide analyser comes down to the implementation of an appropriate site specific preventative maintenance scheme. It should be noted that the daily preventative tasks are not onerous and that for operations that do have high reliability and accuracy, activities take no more than about 20 - 30 minutes per day. The most common causes observed in recent times for poor reliability and accuracy of on-line cyanide analysers can be reduced down to three key areas:

1. Poor filtration.
2. Poor condition of electrodes in titration cell.
3. Incorrect settings and more importantly knowledge of how the settings can influence the accuracy of the result.

The same or similar issues are encountered with all the commercial online cyanide analysers.

#### 3.2.1. Filtration

Experience has shown that most sites which experience poor short term reliability and accuracy with the Orica OCM5000 free cyanide analyser have well below optimum filtration rates and should always be the first place to investigate when it is believed there are errors with the analyser readings. Operations have been observed to experience reduced readings by as much as 40 %, believed to be due to volatilisation of the cyanide in the sampling line and reservoir. Much lower readings are obtained if insufficient filtrate is attained in the reservoir for the titre volume needed. Blocking of the filter is highly dependant on the slurry particle size distribution and properties, particularly clay content. The low rate of filtration and excessive aeration also promotes the formation of scale which has shown to affect both the accuracy and the precision of the analyser by partially or totally blocking filtrate lines. As a general rule of thumb, to maintain optimum filtration the filters should be cleaned of any solids build up at the beginning of each shift by the operators, and on a weekly basis removed for further cleaning in acid followed by cleaning in an ultrasonic bath. Operations using analysers in an hyper saline environment, solutions that have a high scaling tendency or highly viscous slurries will need to at least double the frequency of cleaning to maintain optimum rates of filtration, which is typically >1 mL/sec.

As a general guide the filter of choice is a stainless steel sintered filter with a nominal aperture of 10  $\mu\text{m}$ . This filter in all cases provides a very clean filtrate however is prone to blockages more

easily than the alternative, which is a cloth filter with nominal aperture of 20  $\mu\text{m}$ . Cloth type filters have been shown to be more beneficial in viscous slurries. Trials of alternative cloth material in different configurations and filter mediums are currently being explored with initial success being experienced with a very cost effective sock type system.

Other key variables for optimum filtration to be mindful of are:

- Keep the sample lines as short as possible, i.e. <20 m. If greater than 20 m then investigate the use of a pumping system to transfer slurry to a dedicated hopper adjacent to the analyser hut.
- Air back flush valve is operational and operating at >200 kPa.

### 3.2.2. Titration Cell

The biggest cause observed for poor longer term (weeks) accuracy and/or precision in online potentiometric analysis is poor condition of the electrodes. Typically, it is the reference electrode that is in a poor condition with some cases highlighting that the reference electrode has had no maintenance performed on it for over twelve months. The reference electrode is a Ag/AgCl reference that is located in a double junction reference electrolyte. In nearly all cases of poor accuracy and precision, the silver chloride coating has been lost and the electrolyte has been contaminated. These conditions result in the standard potential drifting and a decrease in potential readings observed between the reference and indicator electrode. The end result is that the analyser may no longer detect an endpoint within the potential window and if a default potential is used then there will be a drift in the endpoint.

As a general guide, the titration cell and electrode/electrolyte conditions should be checked on a daily basis and maintained in optimum condition. The reference electrode electrolyte levels should be maintained and regularly (approximately bimonthly depending on conditions) replaced to avoid the build up of contaminants. Alternative reference electrodes (gel and solid state) being trialled for WAD cyanide analysis may prove to be a more reliable alternative. The silver wire needs to be lightly polished on a regular basis to avoid the build up of contaminants and scale.

### 3.2.3. Titration settings

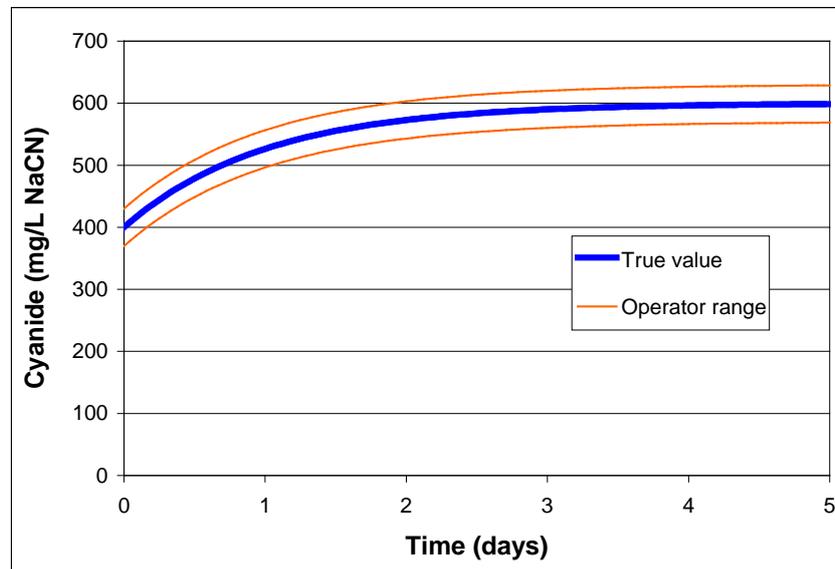
The Orica OCM5000 cyanide analyser (like most potentiometric on-line cyanide analysers) has the ability to detect an endpoint based on a peak in the potential change above a given threshold being identified within a defined potential window. There is also the ability for an endpoint to be defined based on a set default potential. If set, this default potential endpoint is reported by the analyser when no endpoint is detected by the peak detection method.

Typical practice is to set parameters for both peak detection and a default potential based on the potential reading observed for the peak detection method. However, if the peak detection method is unable to identify a peak then the validity of a default potential endpoint would be highly questionable. For example, the most common reason this situation occurs is when the reference electrode potential drifts and hence the set default potential is no longer correct, yet the analyser will still be reporting a result that is now inaccurate and can create significant issues if being used to control cyanide addition. Thus, when using peak detection it is recommended that a default potential should NOT be set as the analyser will then not report a result if no peak is identified and thus will flag an issue with the analyser.

Some operations set the peak threshold high such that the default potential is used. Where there is a difference in the rhodanine titration to the potentiometric endpoint (ie. when copper is present) the rhodanine potential can be used to set the default potential such that comparable results are obtained. However, a clear understanding of the solution speciation and the effect changes in the solution speciation have on the determination are required. There is also no alert from the default endpoint detection method of any issue with the analysis unless the measured starting potential is above the default potential. Thus, close monitoring and cross checking of the online analyser results with laboratory analyses is required to identify when there may be an issue with the online analyser. Hence, operation of analysers using the default potential is not recommended.

#### 4. CYANIDE CONTROL

The residence time of the leach tank in which the cyanide measurement is being taken and the error associated with this measurement, establishes the minimum response time in which changes to the system that produce a change in the cyanide concentration greater than the measurement error can be detected. This minimum response time creates a time lag in providing feedback control to the system. For example, if a leach tank has a 24 hour residence time, the theoretical change in cyanide concentration with a step change in cyanide addition will take several days to be fully realised (Figure 9). Most notable is that in this case only 50 % of the resultant change is observed in the cyanide concentration after 16 hours. If there is an error of  $\pm 30$  mg/L in the cyanide measurement (for complex solutions using the rhodanine method the error would be higher) then at least 12 hours is needed for the change to be outside the operator range. In such a case, it can be seen that changes between individual cyanide analyses conducted on a 3 to 6 hourly basis could be misleading. Thus, it is recommended that a moving average is used to follow the cyanide concentration in the tank to modulate the variability in individual values and establish a clear trend. The control strategy should utilise the cyanide trend and have a minimum of 12 hours pass between making adjustments to the cyanide addition rate (at this point ~40 % of the resultant change will have been observed when all else has remained constant).



**Figure 9: Leach Tank (24 hour residence time) response to a step change in cyanide addition that would result in a change in the measured cyanide concentration from 400 to 600 mg/L NaCN with everything else remaining constant.**

If a large portion of the cyanide addition to the leach circuit is due to ore consumption, small changes in the ore consumption will result in large changes in the measured free cyanide. Thus, with only cyanide addition into the first leach tank it is difficult to control the cyanide addition in order to minimise the cyanide concentration and variability in the leach discharge (and thus minimise the cost of cyanide destruction if implemented). The major cyanide consumption of an ore typically occurs in the first leach tank, thus implementing cyanide measurement along with controlled cyanide addition on the next or subsequent leach tank can substantially reduce the cyanide variability in the leach discharge. In this situation the cyanide addition to the first leach tank can be reduced which has the economic benefit of essentially eliminating cyanide overdosing (increased reagent costs). This also minimises gold losses to tails that would otherwise occur when cyanide is under dosed in the first tank.

## 5. CONCLUSION

This paper has discussed a number of issues that appear to have impaired the uptake of potentiometric on-line cyanide measurement to control cyanide addition within the gold industry. These include a poor understanding of the potentiometric and rhodanine analysis methods, poor reliability of the analyser, and/or an inadequate control strategy.

Understanding the effect of solution composition (eg. presence of copper or zinc) on the silver nitrate titration with potentiometric or rhodanine endpoint detection is vital in interpreting the difference between these two determinations for complex solutions. In such solutions the potentiometric endpoint provides an accurate determination of the "free" cyanide concentration available to readily leach gold.

Most importantly, a maintenance schedule must be established for the online analyser and adhered to if reliable results are to be maintained. Peak detection is recommended with no default potential set, in which case any issues with the analyser become apparent when no result is output. Using the default potential is not recommended unless close monitoring and cross checking is conducted with laboratory analysis.

Using an online cyanide measurement for the control of cyanide addition requires a good understanding of the analysis error/variability and system residence time relative to the frequency of analysis. Where a large portion of the cyanide added is consumed, then a second cyanide measurement and addition point will allow for better control and optimal cyanide addition.

## 6. ACKNOWLEDGEMENTS

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