Measurement of weak and dissociable (WAD) cyanide with a modified potentiometric titration

M. Botz
Elbow Creek Engineering, Billings, MT

E. Milosavljevic
Newmont Mining Corporation, Denver, CO

I. Ward
Kinross Gold Corporation, Toronto, ON

Abstract

The silver nitrate titration method is a rapid and acceptably accurate means of analyzing for cyanide in leach solutions that contain primarily free cyanide. However, in leach solutions containing elevated levels of copper, the titrimetric method overestimates the concentration of free cyanide and underestimates the concentration of weak and dissociable (WAD) cyanide. The authors have developed a modified potentiometric (MP) titration method for determining WAD cyanide that overcomes issues associated with high copper levels in solution. The new MP-WAD method involves addition of a chemical ligand to the sample prior to silver nitrate titration to release cyanide bound to copper. Once released from copper, cyanide in solution is no longer affected by the presence of copper, and titration results are quantitative rather than empirical. In multiple laboratory trials with synthetic solutions and complex actual leach solutions, analytical results obtained with the new MP-WAD method were found to be within about ±5% of analyses obtained with the USEPA OIA-1677 WAD cyanide analytical method.

Introduction

The silver nitrate titration method is widely used to estimate the concentration of cyanide in leach solution for purposes of cyanidation process control. Cyanide determined by silver nitrate titration is commonly referred to as "free" cyanide, but frequently should be referred to as "titratable" cyanide. By definition, free cyanide is the sum of the concentrations of aqueous hydrogen cyanide $HCN_{(aq)}$ and the cyanide anion CN^- (ASTM, 2010). Titration will only yield a reasonably accurate measurement of free cyanide when metal-cyanide complex concentrations (e.g., cadmium, copper, mercury, nickel, silver and zinc) in solution are low. In other words, titration will only yield a reasonably accurate measurement of free cyanide if the solution primarily contains free cyanide.

In cases where metals such as cadmium, copper, mercury, nickel, silver and/or zinc are present in solution, titration will quantify free cyanide plus some portion of cyanide associated with the metals. The most prevalent metals in leach solutions are copper and zinc, which can be present at concentrations ranging

from a few mg/L up to several hundred mg/L. Concentrations of cadmium, mercury, nickel and silver are often less than a few mg/L and are normally not of significant concern relative to measuring cyanide concentrations in leach solutions.

Zinc-cyanide complexes are fully titrated by silver nitrate provided the sample pH is above about 12 (Breuer et al., 2011). If a solution containing only free cyanide and zinc-cyanide complexes is titrated with silver nitrate, all cyanide in the sample will be quantified, not just the free cyanide. Reference to the titration result as "free" cyanide in this case would be incorrect, since both the free cyanide and the zinc-cyanide complexes would have been titrated. For completeness, the results should be referred to as "titratable" cyanide and should be reported along with the analyzed concentration of zinc.

Copper-cyanide complexes are partially titrated by silver nitrate (Mudder et al., 2001; Dai et al., 2005; Breuer and Rumball, 2007). Titration of a solution containing free cyanide and copper-cyanide complexes will result in complete quantification of free cyanide, plus a variable portion of cyanide associated with copper. Titration of solutions containing elevated levels of copper will not yield accurate results for free cyanide nor will all cyanide associated with copper be quantified. Conventional

titration of solutions containing elevated levels of copper is not a recommended technique for quantification of cyanide, due to the variable and partial titration of copper-cyanide complexes that occurs. Lu et al. (2002) provides a thorough review of copper-cyanide chemistry, while Breuer et al. (2011) further discuss issues related to silver nitrate titration for quantification of cyanide.

As an example to illustrate the issue with copper, the authors analyzed a synthetic free cyanide solution and a synthetic copper-cyanide solution using a variety of analytical methods. The synthetic free cyanide solution was prepared with deionized water and reagent-grade NaCN to a calculated concentration of 82 mg/L CN. Conventional colorimetric (visual) titration of the free cyanide solution with silver nitrate yielded an analytical result of 83 mg/L. Conventional potentiometric titration of the free cyanide solution with silver nitrate yielded a result of 84 mg/L, while analysis using the USEPA OIA-1677 (USEPA, 1999) cyanide analytical method yielded a result of 82 mg/L. These results are all in agreement and were not unexpected, since the solution contained only free cyanide.

The synthetic copper-cyanide solution was prepared with deionized water and reagent-grade NaCN and CuCN to calculated concentrations of 125 mg/L CN and 100 mg/L Cu (CN:Cu molar ratio of 3.05:1). Conventional colorimetric (visual) titration of the copper-cyanide solution with silver nitrate yielded an analytical result of 41 mg/L CN. Conventional potentiometric titration of the copper-cyanide solution with silver nitrate yielded a result of 44 mg/L, while analysis using the USEPA OIA-1677 cyanide analytical method yielded a result of 125 mg/L. These results vary widely but were not unexpected, given the known interference of copper to conventional silver nitrate titrations. Calculation of the speciation of copper and cyanide in this solution using thermodynamic equilibria relations indicated the actual free cyanide concentration was approximately 3 mg/L. Use of conventional titration results in this case would have indicated a free cyanide concentration substantially higher than actually present.

The primary challenge with analytical results obtained by conventional silver nitrate titration is their interpretation when copper is present in solution. As illustrated above, conventional titrations do not yield results reflecting the free cyanide concentration when copper is present at an appreciable level. For this reason, results obtained by conventional silver nitrate titration are best termed "titratable" cyanide and should be understood to be empirical rather than quantitative. This is important to consider when calculating cyanide mass balances or leach consumptions if only titratable cyanide analyses are available. Process issues associated with copper in leach solution are discussed by Adams (1999) and Botz et al. (2011).

The issue with copper interference in the silver nitrate titration for cyanide has been known for some time (Hedley and Tabachnick, 1958), but is perhaps not widely acknowledged when interpreting analytical results. Breuer and Rumball (2007) presented a method of estimating copper concentrations from potentiometric titrations, although cyanide was determined as the "titratable" concentration and not the free cyanide or WAD cyanide concentration. Breuer et al. (2011) investigated potentiometric cyanide titrations in regard to the multiple endpoints generated during silver nitrate addition. With copper-cyanide solutions, endpoints of varying intensity were observed and a technique for resolving cyanide concentrations from these endpoints was presented. It appears the use of this technique would require evaluation of individual titration curves by a trained analyst to resolve the various endpoints and extract those relevant to determining cyanide concentrations.

The primary objective of the present work was to modify the conventional silver nitrate titration method such that cyanide associated with copper could be fully quantified. With a modification of this sort, titration would yield analytical results that include free cyanide, plus all cyanide associated with copper and zinc. Since copper and zinc are the dominant metals in most leach solutions, these are the metals of focus in this work.

## Potentiometric silver nitrate titration method

Some basic background information on the potentiometric silver nitrate titration method is useful to facilitate understanding of the newly developed cyanide analytical method. Further information on the potentiometric titration method for analyzing cyanide is presented by Pohlandt et al. (1983), Bott (2000) and Breuer et al. (2011).

When silver nitrate is added to a cyanide-containing solution, silver reacts with "titratable" cyanide to form the soluble silver-cyanide complex:

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^- \qquad (1)$$
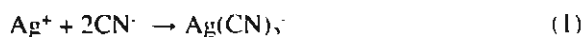
Silver (from silver nitrate) will react with free cyanide, cyanide bound to zinc-cyanide complexes and a portion of cyanide bound to copper-cyanide complexes. When all "titratable" cyanide has reacted with silver, a slight excess of silver will develop in solution, and this excess of silver can be used to signal the endpoint of titration. The titration endpoint is commonly determined visually using the colorimetric indicator "rhodanine" (5-(4-dimethylaminobenzylidene)-rhodanine), which changes from a yellow color to a pink-orange color in the presence of excess silver. Potassium iodide may also be used, which forms the insoluble yellow solid of silver iodide when excess silver is present in solution.

The endpoint of a silver nitrate titration can also be determined potentiometrically. An advantage of potentiometric cyanide determination is the elimination of subjectivity in identifying color change at the titration endpoint. Potential measurements are made using a bare silver working electrode (Ag^0) that exhibits a potential in cyanide solution as silver is leached from the electrode according to the following reaction:

$$Ag^0 + 2CN^- \rightarrow Ag(CN)_2^- + e^- \qquad (2)$$
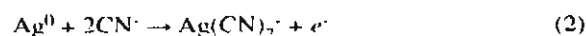
The potential of the bare silver working electrode is measured relative to a silver/silver chloride (Ag/AgCl) reference electrode. As silver nitrate is added to solution according to Eq. (1), the potential slowly increases due to the loss of cyanide through complexation with silver to form silver-cyanide. At the titration endpoint, there is a rapid rise in the potential as all cyanide reactive toward the silver electrode has been consumed by silver. The inflection point in this rapid rise in potential signals the endpoint of the titration.

An example titration curve obtained with a synthetic free cyanide solution is shown on Fig. 1. As silver nitrate is added during a titration, the measured potential forms an "S" curve and the endpoint of the titration occurs at the inflection point in the curve. The inflection point is readily identified by plotting the first derivative (slope) of the titration curve. Data on Fig. 1 correspond to a measured cyanide concentration of 102 mg/L, which compares well with the calculated cyanide concentration of 100 mg/L for the synthetic free cyanide solution.

When copper is present in solution, the reliabilities of colorimetric and conventional potentiometric titration results are impacted. An example titration curve obtained by conventional potentiometric titration of a synthetic copper-cyanide solution is shown on Fig. 2. The shape of this titration curve is significantly different than the curve shown on Fig. 1, and multiple

endpoints are indicated. The calculated cyanide concentration in this synthetic copper-cyanide solution was 1,433 mg/L along with 1,000 mg/L Cu (calculation concentration based on masses of reagents used to prepare the solution). The three peaks shown on Fig. 2 correspond to 156 mg/L, 1,603 mg/L and 2,872 mg/L cyanide, none of which compares well with the calculated cyanide concentration of 1,433 mg/L. The results on Fig. 2 illustrate the difficulty of analyzing copper-cyanide solutions using the conventional silver nitrate method.

Explanation of WAD cyanide

The newly developed cyanide analytical method is referred to as the modified potentiometric (MP) weak and dissociable (WAD) method, or MP-WAD method. The term "WAD cyanide" can be used in reference to either "weak acid dissociable" or "weak and dissociable" cyanide (APHA et al., 1995; ASTM, 2010). This might appear to introduce some ambiguity into the term "WAD cyanide." In practice, however, WAD cyanide analyses using either the "weak acid dissociable" (APHA et al., 1995; ASTM, 2009) or the "weak and dissociable" method (USEPA, 1999; ASTM, 2010) have been found to yield equivalent analytical results for real-world samples (Milosavljevic et al., 1995). Cyanide associated with the stable metal-cyanide complexes of cobalt, iron and gold is not quantified by free cyanide or WAD cyanide analytical methods. In this work, WAD refers to "weak and dissociable" cyanide, since the newly developed analytical method does not involve acidification of samples during analysis. Information about analytical methods available to measure cyanide is listed on the International Cyanide Management Code website (www.cyanidecode.org). Pohlandt et al. (1983) also provide a survey of analytical methods useful for determining cyanide in process solutions and effluents.

With the present extent of development, the MP-WAD method was found to provide accurate measurements of WAD cyanide in synthetic and actual leach solutions containing elevated levels of copper. In view of this, the method is envisioned as a replacement only to the conventional silver nitrate titration method in order to overcome issues associated with copper interference. As will be shown, the method was found to provide a relatively simple means to rapidly measure the concentration of WAD cyanide in synthetic and actual leach solutions.

At present, the MP-WAD method has not been evaluated with respect to quantifying cyanide associated with cadmium, mercury or nickel, and this is a recognized weakness of the method. However, these metals are typically present in low concentrations in leach solution and often do not appreciably contribute to the WAD cyanide concentration. It is also apparent
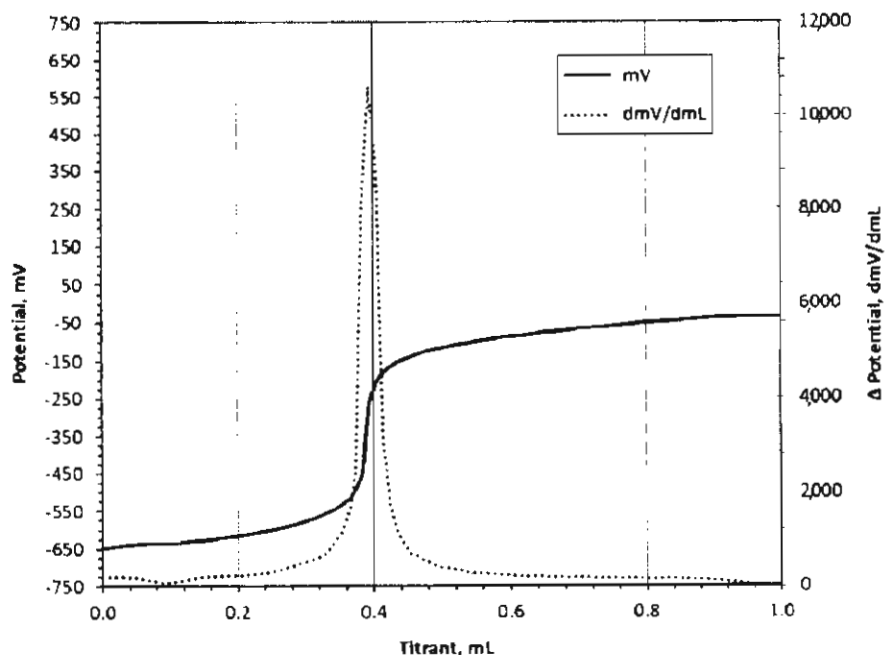

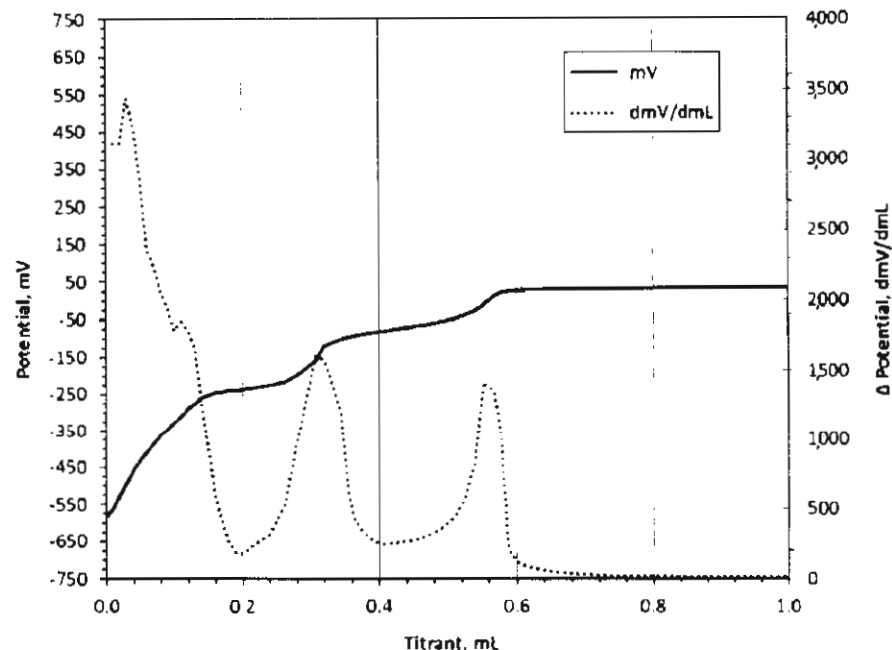Figure 1 — Conventional potentiometric titration of synthetic free cyanide solution.

Figure 2 — Conventional potentiometric titration of synthetic copper-cyanide solution.

the method will not quantify cyanide complexed with silver, since a silver nitrate titration has no way of further reacting with already-formed silver-cyanide complexes. Further characterization of the MP-WAD method would involve analysis of cadmium-, mercury- and nickel-cyanide solutions to determine its ability to measure the associated cyanide.

Ligand selection

The conventional silver nitrate titration method will continue to be widely used to measure cyanide concentrations in leach solution due to its simplicity, even though its accuracy may be questionable in many cases. To improve the accuracy of the method in cases where solutions contain elevated copper concentrations, the authors propose a modified potentiometric

titration method. With the modified method, a chemical ligand is added to solution prior to silver nitrate titration in order to release cyanide bound to copper. If the chemical ligand is referred to as "L", the simplistic reaction of the ligand with copper-cyanide can be written as:[1]
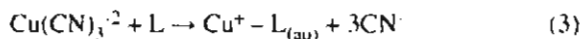
$$Cu(CN)_3^{-2} + L \rightarrow Cu^+ - L_{(aq)} + 3CN^- \qquad (3)$$

Once released from copper, cyanide in solution is no longer affected by the presence of copper, and silver nitrate titration results are quantitative rather than empirical. Addition of a chemical ligand to leach solution samples prior to titration would be a simple modification of the conventional titrimetric method and would permit the measurement of WAD cyanide rather than the empirical "titratable" cyanide.

A significant amount of preparatory work was conducted to identify a ligand exchange reagent (LER) that would react suitably with copper-cyanide complexes but that would not be reactive toward silver-cyanide complexes. Literature reviews of metal-ligand stability constants identified three promising LERs and these were evaluated during preparatory work (which is not reported here):

- N,N'-bis(2-aminoethyl)-1,3-propanediamine
- Tetraethylenepentamine pentahydrochloride
- 2,9-dimethyl-1,10-phenanthroline

Each of these organic polyamines has highly electronegative functional groups known to form chelates with transition metals. It is possible that other organic polyamines, such as triethylenetetramine, might also react with copper-cyanide complexes to release free cyanide into solution, but only the above three ligands were investigated.

Following a large number of potentiometric titration trials, tetraethylenepentamine pentahydrochloride was found to effectively react with copper-cyanide complexes, while not reacting to an observable extent with silver-cyanide complexes. The LER used in all subsequent work was tetraethylenepentamine pentahydrochloride, also known as "TEPA."

For analytical work, a 10 g/L TEPA solution was prepared by dissolving reagent grade tetraethylenepentamine pentahydrochloride (Sigma Aldrich ≥98%) in deionized water. The TEPA solution pH was then adjusted to approximately 12.0 with sodium hydroxide to ensure the pH of samples being titrated remained above 12.0. During preparatory work, a TEPA solution (10 g/L) dosage of 2 μL per each 1 mg/L of copper in the sample per each 1 mL of sample being titrated was found suitable, and this dosage was used in MP-WAD development work. For example, a 1-mL sample aliquot containing 1,000 mg/L copper was titrated after dosing 2,000 μL (2 mL) of TEPA solution (10 g/L) into the sample aliquot.

In cases when the sample copper concentration is unknown, it can be bounded at an upper concentration by assuming all cyanide is complexed with copper in the form $Cu(CN)_2^-$. This species has the highest Cu:CN ratio of the soluble copper-cyanide complexes and would provide a conservative estimate of the copper concentration in solution. The mass ratio of copper to cyanide in this specie is 1.22:1, which means each 1.0 mg/L of CN is associated with at most 1.22 mg/L Cu. For example, a solution with 500 mg/L cyanide could be assumed to contain a maximum of 610 mg/L copper, and this estimated copper concentration could be used to calculate the required TEPA dosage. It is possible in some situations that repeat sample analyses would be required to ensure sufficient TEPA is added in order to fully release cyanide from copper. Overdosage of TEPA to samples being titrated did not appear to affect analytical results (see section "Required LER dosage").

The effect of mixing time following TEPA solution addition to the sample being titrated was not investigated; samples were analyzed within about 1 to 10 minutes following TEPA solution addition. Work to determine the minimum required TEPA dosage was conducted and is discussed later.

Description of samples utilized in testwork

Synthetic cyanide solutions were used in this investigation and the solutions were prepared using deionized water and reagent grade chemicals. The individual effects of copper and zinc on the MP-WAD analytical method were investigated, and synthetic solutions were prepared with reagent grade NaCN (Sigma Aldrich ≥97%), CuCN (Sigma Aldrich ≥99%) and $Zn(CN)_2$ (Sigma Aldrich 98%).

In addition to the synthetic solutions, six samples of actual leach solutions collected from laboratory heap leach columns were used. The actual leach solutions were generated from sulfidic high-copper ores and the sample matrices were relatively complex in that elevated metal levels and a variety of dissolved sulfur species (e.g., thiocyanate, thiosulfate, thionates, etc.) were likely present. Concentrations of cyanide and metals in the actual leach solutions are listed in Table 1. Zinc analyses for the samples were not available. These relatively complex solutions were selected to evaluate performance of the MP-WAD method in "real-world" sample matrices in an effort to determine the industrial utility of the method.

Analytical equipment

Titration equipment. A Schott TitroLine Alpha Plus programmable automatic titration instrument was used for this work. The titrator was controlled from a laptop computer using Schott TitriSoft 2.73 interface software. The titrator was operated with silver nitrate titrant (0.1 M $AgNO_3$), a Schott combination Ag^0 working electrode and a Ag/AgCl reference electrode. Analytical data from the titrator were exported as tables of mL titrant addition versus mV potential measured between the working and reference electrodes. Titration endpoints were identified from the inflection point on the curve of mL titrant addition versus mV potential.

Flow injection analytical equipment. WAD cyanide was analyzed using the flow injection ligand exchange analytical method USEPA OIA-1677 (Milosavljevic et al., 1995; USEPA, 1999). The instrument is owned by one of the authors and was one of the first flow injection ligand exchange instruments constructed in the United States. The instrument was calibrated in the range of 1 to 10 mg/L using three free cyanide standards and samples were diluted (if necessary) prior to analysis to ensure results were determined within the calibration range. All analyses with the instrument were conducted in duplicate with the average value reported.

Analytical results

A variety of synthetic solutions were analyzed with the

---

[1] The dominant copper-cyanide complex in most leach solutions is $Cu(CN)_3^{-2}$, though the $Cu(CN)_2^-$ and $Cu(CN)_4^{-3}$ complexes can also be present at appreciable concentrations. In copper-cyanide solutions, all three of these complexes are simultaneously present, though some complexes may have only minor concentrations.

MP-WAD method to evaluate the individual effects of copper and zinc on analytical results. Synthetic solutions were prepared by diluting small aliquots of concentrated metal-cyanide stock solutions (1 g/L of copper or zinc) and concentrated cyanide stock solution (1 g/L CN) to yield the final desired chemistry for each of the synthetic solutions. The concentrated stock solutions were analyzed by the MP-WAD method and the USEPA OIA-1677 method to determine WAD cyanide prior to preparing synthetic solutions. Results of the analyses of the concentrated stock solutions are listed in Table 2. Analytical results shown in Table 2 for the MP-WAD and OIA-1677 methods are in good agreement for the free cyanide, copper-cyanide and zinc-cyanide stock solutions. Analyzed WAD cyanide concentrations for the solutions are all within ±6% of the calculated cyanide concentration.

Analysis of free cyanide solutions. Two synthetic free cyanide solutions were analyzed with the MP-WAD method, and the results are listed in Table 3. With both of the free cyanide solutions, differences between calculated and analyzed cyanide concentrations are less than 4%. These results were expected, since the synthetic solutions did not contain copper as an interference and silver nitrate titration is known to be an accurate means of measuring the concentration of free cyanide. The results also demonstrate that LER addition does not affect analytical results by reacting with silver added during titration. If the LER were to react with silver, it would not be possible to obtain reliable analytical results using the MP-WAD method.

Analysis of copper-cyanide solutions. Four synthetic copper-cyanide solutions were analyzed with the MP-WAD method and results are listed in Table 4. The synthetic solutions each contained 200 mg/L cyanide, but with copper concentrations ranging from 10 mg/L to 139.6 mg/L. With all of the samples, differences between calculated and analyzed cyanide concentrations are less than 3%. These results demonstrate the ability of the MP-WAD method to accurately measure the concentration of WAD cyanide in samples containing a range of copper concentrations.

To illustrate the effect of LER addition on the potentiometric titration of cyanide, the same synthetic copper-cyanide solution analyzed by conventional potentiometric titration (Fig. 2) was analyzed by the MP-WAD analytical method. This sample contained 1,433 mg/L cyanide and 1,000 mg/L copper and was found to yield inaccurate results when analyzed with the conventional silver nitrate titration method (Fig. 2). In contrast, when this same sample was analyzed by the MP-WAD method, a single clearly discernible titration endpoint was generated, which is shown on Fig. 3. The titration endpoint corresponds to a cyanide concentration of 1,488 mg/L. This compares favorably with

the calculated cyanide concentration of 1,433 mg/L, the difference being about 3.8%. Analysis of this copper-cyanide solution by the OIA-1677 method yielded a result of 1,379 mg/L, also a difference of about 3.8% from the calculated cyanide concentration of 1,433 mg/L.

Table 1 — Chemistry of actual leach solution samples.					
Sample No.	CN (mg/L)*	Ag (mg/L)	Cu (mg/L)	Fe (mg/L)	Zn (mg/L)
1	640	0.02	236	7.85	No analysis
2	260	0.05	602	8.15	No analysis
3	400	0.06	1,254	12.3	No analysis
4	770	0.1	177	8.55	No analysis
5	720	0.18	260	10.6	No analysis
6	160	0.01	588	168	No analysis

* Analyzed by conventional colorimetric silver nitrate titration by a commercial laboratory.

Table 2 — Analysis of concentrated stock solutions.					
Stock solution	Calculated* copper (mg/L)	Calculated* zinc (mg/L)	Calculated* CN-WAD (mg/L)	OIA-1677 CN-WAD (mg/L)	MP-WAD CN-WAD (mg/L)
Free cyanide	0	0	1,000	1,060	999
Copper-cyanide	1,000	0	1,433	1,379	1,441
Zinc-cyanide	0	1,000	1,990	2,080	1,931

* Calculated based on mass of reagent chemicals used to prepare stock solutions.
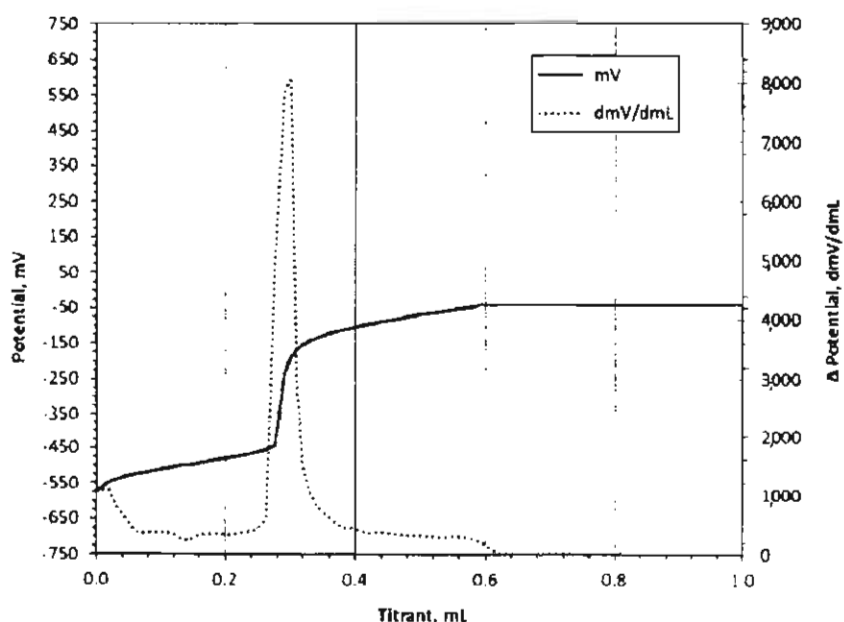

Figure 3 — MP-WAD potentiometric titration of synthetic copper-cyanide solution.

Table 3 — Analysis of synthetic free cyanide solutions.			
Sample	Calculated* cyanide (mg/L)	MP-WAD/ CN-WAD (mg/L)	Difference (%)
1	10.0	9.67	3.4%
2	200.0	200.7	0.3%

* Calculated based on mass of reagent chemicals used to prepare synthetic solutions.

Table 4 — Analysis of synthetic copper-cyanide solutions.

Sample	Calculated* Copper (mg/L)	Calculated* Cyanide (mg/L)	MP-WAD CN-WAD (mg/L)	Difference (%)
1	10.0	200.0	194.8	2.7%
2	50.0	200.0	195.0	2.6%
3	100.0	200.0	195.0	2.6%
4	139.6	200.0	201.0	0.5%

* Calculated based on mass of reagent chemicals used to prepare synthetic solutions.

Table 5 — Analysis of synthetic zinc-cyanide solutions.

Sample	Calculated* zinc (mg/L)	Calculated* cyanide (mg/L)	MP-WAD CN-WAD (mg/L)	Difference (%)
1	10.0	200.0	193.9	3.1%
2	50.0	200.0	194.3	2.9%
3	105.0	200.0	193.9	3.1%

* Calculated based on mass of reagent chemicals used to prepare synthetic solutions.

Table 6 — Analysis of synthetic zinc-cyanide solutions.

Calculated* zinc (mg/L)	Calculated* cyanide (mg/L)	MP-WAD CN-WAD (mg/L)		Difference (%)
		With LER	Without LER	
105.0	200.0	194.3	190.8	1.8%

* Calculated based on mass of reagent chemicals used to prepare synthetic solutions.

Analysis of zinc-cyanide solutions. Three synthetic zinc-cyanide solutions were analyzed with the MP-WAD method and results are summarized in Table 5. The synthetic solutions each contained 200 mg/L cyanide, but with zinc concentrations ranging from 10 mg/L to 105 mg/L. With all of the samples, differences between calculated and analyzed cyanide concentrations are less than 4%. These results demonstrate the ability of the MP-WAD method to accurately measure the concentration of WAD cyanide in samples containing a range of zinc concentrations.

It is known zinc-cyanide complexes are fully titratable by silver nitrate without LER addition, provided the sample pH is above about 12.0. To confirm this with the MP-WAD method, an additional potentiometric titration was conducted with a synthetic zinc-cyanide sample but without LER addition. The result from this titration without LER addition is compared in Table 6 against the result where LER was used. As indicated, analytical results differ by less than 2% between the samples with and without LER addition. These data confirm zinc-cyanide complexes are titrated by silver nitrate with or without LER addition, but also the data confirm the LER does not react with zinc-cyanide complexes such that analytical results are affected.

Analysis of actual leach solutions. The six actual leach solution samples listed in Table 2 were analyzed by the MP-WAD method and the OIA-1677 method and results are listed in Table 7. The actual leach solution samples contained 177 to 1,254 mg/L of copper along with varying levels of silver and iron (zinc was not analyzed in the samples). As listed in Table 7, cyanide analyses conducted by conventional silver nitrate

titration yielded results ranging from 160 mg/L to 770 mg/L for "titratable" cyanide.

Cyanide analytical results listed in Table 7 show consistency between results obtained with the MP-WAD and OIA-1677 methods, the differences being about 1.8% to 5%. Data in Table 7 demonstrate the ability of the MP-WAD method to analyze for WAD cyanide, even in complex actual leach solutions. In comparison to the well-developed USEPA OIA-1677 method, the MP-WAD method yields analytical results that appear, at least for practical purposes, to be sufficiently accurate at cyanide concentrations of importance in leach solutions.

Of particular note regarding data in Table 7 are the cyanide concentrations determined by conventional silver nitrate titration. Differences in results obtained by conventional colorimetric titration versus the MP-WAD and OIA-1677 methods range from about 12% (sample number 4) to 82% (sample number 6). This finding highlights the drawback of using conventional silver nitrate titrations when analyzing solutions containing elevated levels of copper. Conventional silver nitrate titration results reported in Tables 2 and 7 do not reflect the actual free cyanide or WAD cyanide concentrations in the samples and have little utility in quantifying cyanide available for leaching or for calculating cyanide consumptions.

Required LER dosage

For MP-WAD cyanide titration results presented in the preceding sections, LER addition to the samples being titrated was generally 2 μL (10 g/L TEPA solution) per each 1 mg/L copper in the sample, per each 1 mL of sample being titrated. To quantify the minimum amount of LER required to fully release copper from its cyanide complexes, a series of titrations was conducted with increasing dosages of LER to individual 1-mL aliquots of a sample. The concentrated copper-cyanide stock solution was selected for this work (1,433 mg/L CN and 1,000 mg/L Cu). Results from the MP-WAD titrations are listed in Table 8 and shown in Fig. 4. Data in Table 8 and Fig. 4 indicate that at a dosage between 0.86 and 1.28 mole LER per mole copper, the difference between calculated and analyzed WAD cyanide concentrations decreases to about 5% or less. Interpolating from Fig. 4, it appears the minimum stoichiometry for LER addition is about 1.0 mole of TEPA (hydrochloride form) per mole of Cu. As indicated in Fig. 4, overdosing LER up to about 3.5 moles TEPA per mole of Cu does not appear to adversely affect analytical results.

Estimated detection limit

To gauge the approximate detection and quantitation limits for the MP-WAD cyanide analytical method, a portion of the procedure published by the USEPA was followed (USEPA, 1986). The detection limit is the minimum concentration that can be reliably reported, while the quantitation limit is the minimum concentration that can be reliably quantified. The USEPA procedure was not followed in its entirety, since the objective was to conduct only a preliminary evaluation of the approximate detection and quantitation limits. It is not intended that the MP-WAD method serve to measure very low levels of cyanide, but rather it is intended the method be used to measure cyanide at concentrations of importance in leach solutions.

Derivation of detection and quantitation limits involves conducting several replicate analyses of the same solution and

calculating the standard deviation (SD) of the results. The detection limit (DL) and quantitation limit (QL) are then calculated as follows for the case where seven replicate analyses are conducted:

$$DL = SD \times 3.143 \qquad (4)$$

$$QL = SD \times 10 \qquad (5)$$

The significance of the above calculations is discussed in USEPA (1986). Actual leach solution sample No. 3 (see Table 2) was analyzed for this work to provide a real-world matrix, as opposed to analyzing a high-purity reference standard where common interferences are absent. The actual leach solution sample was first diluted 500:1 with deionized water to yield a diluted sample with a cyanide concentration of about 4 mg/L. The concentration of about 4 mg/L was within the quantitation limit range of about 1 to 5 mg/L estimated by the authors prior to conducting the work. A 0.025-M silver nitrate titrant solution was used to increase the sensitivity of the potentiometric titration. Results from the seven replicate analyses are listed in Table 9. This work in no way represents an exhaustive evaluation of the MP-WAD method detection or quantitation limits, but was intended to serve as a derivation of preliminary values. Further work would be required to establish firm detection and quantitation limits for the analytical method (see USEPA, 1986 for details).

The preliminary detection limit calculated for the MP-WAD method is about 0.5 mg/L, while the preliminary quantitation limit is about 1.7 mg/L. This is consistent with the experience of the authors, who consider the silver nitrate titration method to be generally valid for cyanide concentrations above about 1 mg/L. It is possible the detection limit and the quantitation limit could be lowered by using a more dilute silver nitrate titrant solution and/or by using a lower concentration of cyanide in the solution being analyzed.

Table 7 — Analysis of actual leach solutions.

Sample	MP-WAD CN-WAD (mg/L)	OIA-1677 CN-WAD (mg/L)	Difference (%)	Titratable* cyanide (mg/L)
1	783	824	5.0%	640
2	1,109	1,129	1.8%	260
3	2,024	1,944	4.1%	400
4	905	879	3.0%	770
5	1,018	987	3.1%	720
6	852	868	1.8%	160

* Conventional colorimetric silver nitrate titration performed by a commercial laboratory.

Table 8 — Effect of varying LER addition to copper-cyanide stock solution.

LER addition (mole/mole Cu)	Calculated* cyanide (mg/L)	Calculated* copper (mg/L)	MP-WAD CN-WAD (mg/L)	Difference (%)
0.00	1,433	1,000	689	51.9%
0.43	1,433	1,000	947	33.9%
0.86	1,433	1,000	1,296	9.6%
1.28	1,433	1,000	1,509	5.3%
1.71	1,433	1,000	1,462	2.0%
2.57	1,433	1,000	1,478	3.1%
3.42	1,433	1,000	1,503	4.9%

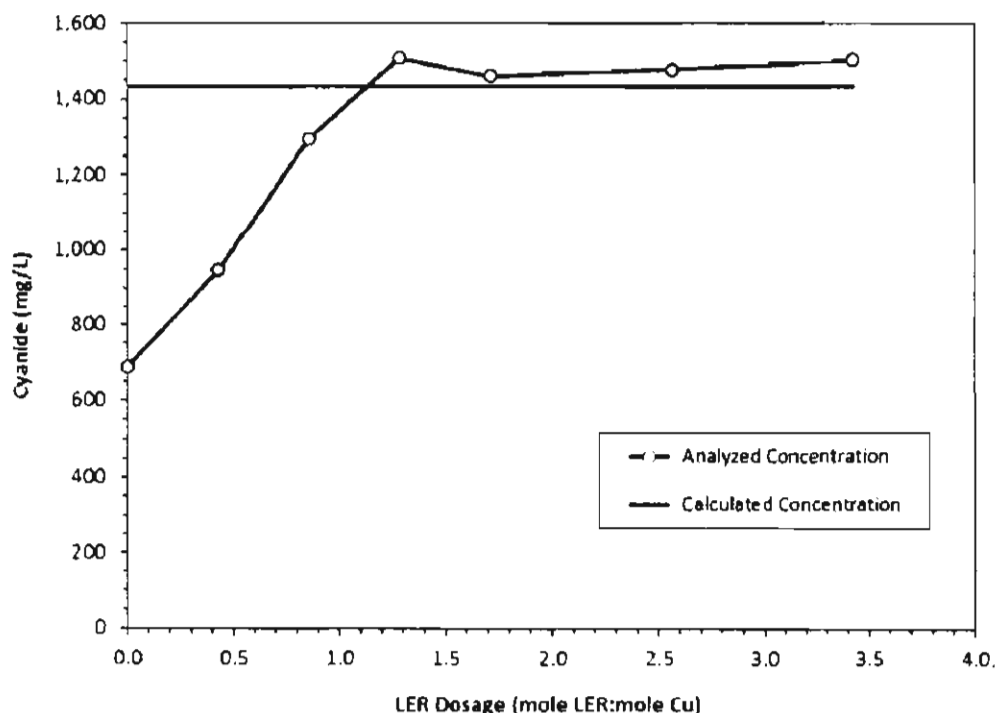* Calculated based on mass of reagent chemicals used to prepare stock solution.

Figure 4 — Effect of varying LER addition to copper-cyanide stock solution.

Summary and conclusions

The newly developed MP-WAD cyanide analytical method has been demonstrated in the laboratory to provide accurate measurements of WAD cyanide in samples containing elevated levels of copper and zinc. This has been done using a variety of synthetic cyanide solutions and complex actual leach solutions. The key to development of the MP-WAD method was identification of the ligand exchange reagent tetraethylenepentamine pentahydrochloride (TEPA), which was found to react with copper-cyanide complexes but not with silver-cyanide complexes. Analytical results obtained with the MP-WAD method were found to be within about ±5% of analyses obtained with the flow injection ligand exchange method USEPA OIA-1677. The MP-WAD method provides an

accurate, rapid and inexpensive measurement of WAD cyanide at concentrations of importance in leach solutions.

It should be recognized the MP-WAD method will not report cyanide bound to silver, since silver nitrate addition to a silver-cyanide solution would not have any effect on the already-formed silver-cyanide complex. Additional investigation of the MP-WAD method with cadmium-, mercury- and nickel-cyanide complexes is needed to evaluate the ability to measure cyanide associated with these complexes.

The MP-WAD method is not likely suitable for accurately measuring cyanide at concentrations less than about 1 mg/L and is not envisioned as a replacement for the OIA-1677 method. The OIA-1677 method is suitable for measuring very low cyanide concentrations and is widely used for environmental monitoring purposes. The MP-WAD method does provide a lower-cost alternative to measuring WAD cyanide in leach solution at levels above about 1 mg/L using relatively simple equipment that could be readily used and understood at industrial operations. The time required for conducting an MP-WAD analysis is comparable to the OIA-1677 method, which is about three to five minutes per sample. The recommended application of the MP-WAD method is for leach solutions containing elevated levels of copper and with cyanide concentrations above about 1 mg/L.

Acknowledgments

References

Adams, M.D., 1999, "Aspects of the chemistry and mineralogy of gold-copper and copper-gold ore processing," Presented at Cretest Colloquium, Western Australia

American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), 1995, Standard Methods for the Examination of Water and Wastewater, 19th Edition, Washington, D.C.

ASTM (American Society for Testing and Materials), 2009, "Standard test methods for cyanides in water," ASTM International Standard D2036

ASTM (American Society for Testing and Materials), 2010, "Standard Guide for Understanding Cyanide Species," ASTM International Standard D6696

Bott, A.W., 2000, "Electrochemical titrations," Current Separations, Vol. 18, No. 4, pp. 129-132.

Botz, M.M., Fleming, C.A., and Ford, K.J.R., 2011, "Cyanide leaching of gold-copper porphyries: chemistry and challenges," Presented at World Gold, Montreal, Canada.

Breuer, P.L., Sutcliffe, C.A., and Meakin, R.L., 2011, "Cyanide measurements by silver nitrate titration: comparison of rhodanine and potentiometric endpoints," Hydrometallurgy, Vol. 106, Issues 3-4, pp. 135-140

Breuer, P.L., and Rumball, J.A., 2007, "Cyanide measurement and control for complex ores and concentrates," Proceedings Ninth Mill Operators' Conference, Freemantle, WA, Australia, pp. 249-254

Dai, X, Jeffrey, M.I. and Breuer, P.L., 2005, "The development of a flow injection analysis method for the quantification of free cyanide and copper cyanide complexes in gold leaching solutions," Hydrometallurgy, Vol. 76, Issues 1-2, pp. 87-96

Hedley, N., and Tabachnick, H., 1958, Mineral Dressing Notes, American Cyanamid Company, New York

Lu, J., Dreisinger D.B., and Cooper, W.C., 2002, "Thermodynamics of the aqueous copper-cyanide system," Hydrometallurgy, Vol. 66, pp. 22-36

Milosavljevic, E.B., Solujic, L.J. and Hendrix, J.L., 1995, "Rapid distillationless 'free cyanide' determination by a flow injection ligand exchange (FI/LE) method," Env. Sci. Tech., Vol 29, pp. 426-430

Mudder, T.I., Botz, M.M., and Smith, A., 2001, Chemistry and Treatment of Cyanidation Wastes, 2nd Edition, Mining Journal Books, London

Pohlandt, C., Jones, E.A., and Lee, A.F., 1983, "A critical evaluation of methods applicable to the determination of cyanides," Journal of the South African Institute of Mining and Metallurgy, Vol. 83, pp. 11-19

USEPA, 1986, Code of Federal Regulations (CFR), Title 40, Part 136, Appendix B, "Definition and procedure for the determination of the method detection limit," Revision 1.11.

USEPA, 1999, "Method OIA-1677 Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry," Document EPA 821-R-99-013

Table 9 — Results from replicate analyses of diluted actual leach solution sample No. 3.

Analysis*	MP-WAD/ CN-WAD (mg/L)
1	4.456
2	4.423
3	4.521
4	4.390
5	4.358
6	4.098
7	4.098
Average	4.335
Standard deviation	0.170
Relative standard deviation	3.92%
Detection limit	0.533
Quantitation limit	1.697

* Actual leach solution sample No. 3 (Table 1) diluted 500:1 with deionized water.