DRAFT #2

Test Program to Evaluate

Cyanide Destruction Options Using

SO_2/AIR, CombinOx® and CyPlus Peroxygen - Based Technologies

For the Treatment of Leach Effluents from the

Doris North Project in Canada

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Statement of Confidentiality

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1. EXECUTIVE SUMMARY

To be completed when the capital cost figures become available.

2. SCOPE OF WORK

The present test work program was undertaken at the request of Miramar Mining Corporation to evaluate cyanide destruction options for the treatment of leach effluents from the Doris North Project in Canada. The work included investigations of Caro's Acid, the SO_2/AIR process and CombinOx®. The scope of work was based on the February 2007 agreement and subsequent discussions between CyPlus and Miramar, and included the following:

2.1 Cyanide Destruction Sample Preparation

In the February 2007 agreement, the scope of work included procedures to generate and treat a barren bleed stream. It was subsequently determined that this would not be necessary and all work would be carried out on the "Slurry Backfill Detox Feed Sample" alone. CyPlus followed the CLIENT'S metallurgical instructions for the preparation of the concentrate sample to generate suitable cyanide destruction feed samples using the conditions provided below:

Leach Conditions for Cyanide Destruction Concentrate

Percent solids	35%
pH	10.5(using $Ca(OH)_2$)
Preaeration Step	7 hours(subsequently added)
NaCN addition	1,000 mg NaCN / L solution
Maintained CN level	550 ppm CN_F
Carbon addition	20 g/L slurry
Leach (CIL) time	72 hours

2.1.1 Sample Preparation after Leaching to Produce Slurry Backfill Detox Feed Sample

1. Remove carbon from slurry. Save carbon sample.
2. Add NaCN, if necessary, to produce CN_{WAD} concentration of 625 ppm.
3. The pH will be adjusted to 10.5 with $Ca(OH)_2$.

2.2 Cyanide Destruction Laboratory Program

Testwork will be conducted on CLIENT'S **Backfill Slurry** sample, generated using the conditions described above by a team of CyPlus scientists. The cyanide destruction laboratory program will include the following:

- Continuous cyanide destruction optimization by the SO_2/AIR process to determine the effectiveness of the process to the Backfill Slurry effluent.

- Continuous cyanide destruction optimization by the new CyPlus CombinOx® process(es) to determine the effectiveness of the process(es) to the Backfill Slurry effluent.

- Cyanide destruction optimization by the CyPlus Cold Caro's Acid (peroxymonosulphuric acid) process to determine the effectiveness of the process to Backfill Slurry effluent. In order to accommodate the reagents most likely to be used on-site, 37% sulfuric acid and 50% hydrogen peroxide will be used for the treatment and assessed for the production yield of Caro's acid.

- Chemical characterization of all process feed and residual streams, including CN_{WAD} (using the Picric Acid method), CN_T(calculated using CN_{WAD} result and soluble iron), Cu, Ni, Fe, and pH.

The target(s) of the treatment program will be:

- Weak Acid Dissociable Cyanide < 0.5 ppm CN_{WAD}

For the purpose of "typical" reagent and capital cost estimates, the following conditions will be used:

- 600 ppm CN_{WAD}
- Flowrate of 2.8 dry tonnes/hr. at 40% solids

The "Typical" conditions from the February 2007 agreement, shown above, subsequently changed and "Design" conditions were added. Both are shown in **Section 8** and **Tables 5 and 6**.

2.3 Slurry Samples

This sample, weighing approximately 40 kg, was received at the CyPlus Corporation Piscataway, New Jersey laboratory in late January 2007. The sample was received in good condition and there was no sign of tampering during shipment.

The head sample shipped to CyPlus by Miramar consisted of approximately 40 kg of a flotation concentrate that was produced from a Doris North ore sample made from select diamond drill core for Miramar at the Process Research Associate metallurgical laboratory in Vancouver. This sample was received at the CyPlus

Corporation's Piscataway, New Jersey laboratory in late January 2007 in good condition with no signs of tampering during shipment. This concentrate was then subjected to a cyanide leach at the CyPlus Lab using parameters provided to CyPlus by Miramar's metallurgical consultant to generate a fresh cyanide leach residue for cyanide destruct testing with residual cyanide concentrations comparable to those generated by PRA in the metallurgical testing program (consistent with levels expected in the mill), using conditions described above in **Section 2.1**.

3. PROCESS DESCRIPTIONS

3.1 SO_2/AIR PROCESS

The SO_2/AIR process can be applied to the treatment of both cyanide solutions and pulps, however, it is in the area of slurry treatment (CIP/CIL pulps or re-pulped filtercakes from a Merrill-Crowe circuit) where the process has enjoyed a recognized worldwide reputation. Main advantages of the process are the removal of the total cyanide to levels of about 1 mg/L, in a single-stage continuous reactor and low operating costs.

The technology uses sulfur dioxide (SO_2), in various reagent forms, (sodium sulfite, sodium metabisulfite, ammonium bisulfite, liquid SO_2, and SO_2 containing roaster gas or SO_2 from burning elemental sulfur) in combination with air (or pure oxygen). Stoichiometrically, the process requires a ratio of approximately 2.5 g of SO_2/g of CN_{WAD}. The oxidation of cyanide is in accordance with one of the following overall reactions:

$$CN^- + Na_2SO_3 + O_2 \rightarrow OCN^- + Na_2SO_4$$

or:

$$CN^- + \tfrac{1}{2} Na_2S_2O_5 + O_2 + \tfrac{1}{2} H_2O \rightarrow OCN^- + \tfrac{1}{2} Na_2SO_4 + \tfrac{1}{2} H_2SO_4$$

or:

$$CN^- + SO_2 + O_2 + H_2O \rightarrow OCN^- + H_2SO_4$$

As shown above, the oxidation of cyanide produces cyanate (OCN^-) and, depending on the SO_2 reagent, produces sulfuric acid (H_2SO_4) as an intermediate. At the prevailing pH of the process, however, the sulfuric acid is continuously neutralized with lime producing calcium sulfate dihydrate (gypsum), as follows:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \bullet 2H_2O$$

The process will oxidize free cyanide and all cyanide complexed with copper, nickel, zinc, silver, and cadmium. The oxidation is catalyzed by soluble copper (Cu^{2+}), which, if required, can be supplemented by addition of copper sulfate solution. As cyanide is oxidized, metals are liberated and precipitated out of solution as hydroxides by the following reactions:

$$Me^+ + OH^- \rightarrow MeOH$$

or:

$$Me^{2+} + 2OH^- \rightarrow Me(OH)_2$$

Cyanide present in the form of a strong complex, bound with either iron, cobalt, or gold, is not oxidized by the process. Gold cyanide, of course, should not be a concern for a destruction unit, as it is recovered by carbon within the plant. Removal of the iron and cobalt cyanide complexes is achieved by precipitation with copper or zinc, according to the following reactions:

$$2\ Me^{2+} + Fe(CN)_6{}^{4-} \rightarrow Me_2Fe(CN)_6$$

or:

$$2\ Me^{2+} + Co(CN)_6{}^{4-} \rightarrow Me_2Co(CN)_6$$

Generally, the SO_2/AIR process works best in the pH range of 8 to 9 and optimum operating pH is determined during the test work program. Optimization of both pH operating range and reagent consumption has proven to be site-specific for all ore types tested to date.

Cyanate produced by oxidation of cyanide slowly hydrolyzes to carbonate and ammonium as follows:

$$OCN^- + 2H^+ + H_2O \rightarrow CO_2 + NH_4{}^+$$

or:

$$OCN^- + OH^- + H_2O \rightarrow CO_3{}^{2-} + NH_3$$

depending on pH.

3.2 Hydrogen Peroxide and Caro's Acid

Hydrogen peroxide (H_2O_2) has a well-established reputation as the process of choice for treating clear cyanide solutions. The primary benefit of hydrogen peroxide is that it is a “clean” chemical in the sense that the reaction product of the H_2O_2 itself is simply water. In a peroxide treatment system there will be no appreciable increase in the dissolved solids concentration; scaling and undesirable salting conditions are avoided. This is an important factor in any flowsheet scenario incorporating a filtration stage.

The oxidation of cyanide with peroxide produces cyanate and water as shown in the following equation:

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

The cyanate subsequently hydrolyzes slowly to produce ammonium and carbonate ions:

$$OCN^- + 2H^+ + H_2O \rightarrow CO_2 + NH_4^+$$

or:

$$OCN^- + OH^- + H_2O \rightarrow CO_3^{2-} + NH_3$$

depending on the pH.

Although ammonia (NH_3) is toxic to fish at low levels, it is almost entirely available in the far less toxic cationic form (NH_4^+) at the natural pH of open waterways.

If excess hydrogen peroxide is present in the treated wastewater, it rapidly decomposes to water and oxygen, presenting no environmental threat:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Hydrogen peroxide is capable of oxidizing both "free" cyanide (CN_f) and complexes (titratable cyanide):

$$CN^-, HCN, NaCN, KCN, Ca(CN)_2, Cd(CN)_4^{2-}, Zn(CN)_4^{2-}$$

and “weak acid dissociable” cyanide (CN_{WAD}) complexes, which include the above mentioned titratable cyanide species as well as the following metal cyanide species:

$Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Cu(CN)_4^{3-}$, $Ag(CN)_2^-$, $Ni(CN)_4^{2-}$

In contrast, the following metal cyanide complexes cannot be oxidized by hydrogen peroxide. These compounds, along with CN_{WAD} complexes, are measured as “total” cyanide (CN_{tot}):

$Au(CN)^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$

However, it is still possible to achieve CN_{tot} limits by precipitating the $Fe(CN)_6^{4-}$ with, for example, copper ions:

$Fe(CN)_6^{4-} + 2Cu^{2+} \rightarrow Cu_2Fe(CN)_6$ (solid)

This can normally be accomplished by lowering the pH to 8 to 9 in the presence of copper hydroxide. Occasionally, more copper must be added in the form of copper sulfate to achieve the desired CN_{tot} level.

The cyanide destruction reaction using peroxide is relatively fast in most wastewater samples. The presence of transition metals, especially copper, helps to accelerate the reaction. However, effluents that contain little or no metals may require a catalyst in order to accommodate a treatment circuit with limited effluent retention capabilities. Copper sulfate pentahydrate additions are ideal for this purpose.

Low effluent temperatures will significantly slow down the reaction time. Therefore, cyanide destruction circuits must be designed with sufficient retention time to allow the reaction to go to completion at the lowest possible effluent temperature experienced at a particular site. If shorter retention times are desired, more copper catalyst can be added to reduce the cyanide destruction reaction time.

Hydrogen peroxide can be shipped safely at high concentrations (up to 70% by weight H_2O_2) and stored for long periods of time without appreciable loss of activity, which makes H_2O_2 an ideal choice for remote locations. H_2O_2 has proven invaluable for emergency detoxification programs, where low capital costs and quick start-up are essential requirements.

Caro's Acid, or peroxymonosulfuric acid (H_2SO_5) is simply made from a mixture of hydrogen peroxide and sulfuric acid. Stoichiometrically, the molar ratio of peroxide to H_2SO_4 is 1:1, however, in operating practice, higher additions of acid are the norm. Since Caro's acid is a more powerful oxidizer than hydrogen peroxide, it has proven applicable in the treatment of slurries. In certain cases it can increase the efficiency of the peroxygen/cyanide destruction reaction by quickly oxidizing the free and weak acid dissociable cyanide species to cyanate.

The Caro's acid solution used for the testwork contained in this report is similar to solutions prepared by a CyPlus/Degussa's DegOX® "Cold" Caro's Acid Generator. These generators produce high yield Caro's acid, which has proven to significantly reduce the reagent demand compared to other generators available for the mining industry.

Generation of Caro's acid and oxidation of cyanide follow the basic reactions below:

$$H_2O_2 + H_2SO_4 \rightarrow H_2SO_5 + H_2O$$

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

Reaction products of Caro's Acid oxidation are essentially the same as for the SO_2/AIR process.

3.3 CombinOx®

The new CyPlus CombinOx® process has been developed through the joint efforts of CyPlus GmbH, CyPlus Corp. and Inco scientists under the framework of a cooperation agreement. The main objective of the effort was to provide the industry with a low cost alternate process for cyanide detoxification achieving the same or lower residual cyanide total targets, as has been common for the SO_2/AIR process. The new process uses both sulfur dioxide (in any of the available product forms) and peroxygen chemicals as reagents and takes advantage of certain synergies between the processes to reduce total reagent requirements. Identical end products are obtained as in both background technologies (SO_2/AIR or Caro's). Soluble copper provides the catalyst; dissociated metals are precipitated as hydroxides and strong cyanide complexes are precipitated as insoluble salts, predominantly in the presence of copper or zinc. The new process can offer some or all of the following advantages:

a) Lower Capital Cost

b) Lower Operating Cost

c) Tremendous flexibility towards changes in cyanide loadings due to higher feed cyanide or mill tonnage increase; i.e. the system can take higher cyanide loads without the need to upgrade the installation.

d) The process can be automated for minimal operator attention. Automation is recommended for ease of operation, however, it is not essential to the process.

e) If designed for higher regulatory limits, such as International Cyanide Management Code tailings pond limits, the process can be readily upgraded to achieve lower residual cyanide and metal concentrations if required at any time in the future.

f) "Process Balancing" to accommodate particular reagent shortages within a prevailing market and/or system component breakdowns or maintenance.

Application of the process will be primarily for slurry treatment options and its suitability will be dependent on prevailing metallurgy of the ore as well as a function of local reagent pricing. CombinOx® technology is exclusively marketed by the CyPlus group of companies.

4. ANALYTICAL PROCEDURES

The following briefly describes the analytical methods employed for assaying solution (<0.45 μm) samples.

Filtered solution samples were immediately processed through a spectrophotometric determination of weak-acid dissociable cyanide (CN_{WAD}) using the buffered picric acid method **(see Appendix A)**. Total cyanide (CN_T) was calculated as $CN_{WAD} + 2.795[Fe]$ where [Fe] represents the iron concentration in solution (units of mg/L). Soluble base metal assays (Cu, Ni and Fe) on both feed and treated effluents were analyzed by atomic absorption spectrophotometry (AAS –Perkin Elmer Analyst 200).

5. FEED PREPARATION FOR CYANIDE DESTRUCTION TESTWORK

5.1 Leach and Au/Ag Extraction

During the course of the testwork, six cyanidation leaches were performed, as described in **Section 2.1**. Carbon was used for gold and silver removal during the 72 hour CIL.

5.2 Feed Chemistry

Since the leach solution chemistry can vary with time, the samples were checked for CN_{WAD} and pH before treatment. Based on the CN_{WAD} analysis and the pH reading, sodium cyanide and calcium hydroxide were added to generate an effluent containing approximately the following:

CIP Tails Slurry

Percent Solids	35.0 %
CN_{WAD}	625 ppm
pH	10.5

After adjusting the sample cyanide levels and pH, the sample was once again analyzed for CN_{WAD}, Cu, Fe, Ni and pH. These results are shown in **Tables 1, 2 and 3** as the "Feed" descriptions above each corresponding detoxification test. A calculated CN_T value is also provided.

6. TEST RESULTS

6.1 Test Procedures

The SO_2/AIR process was carried out in continuous mode in a properly aerated and agitated reactor, as would be the case in typical plant operation. Reagents (sodium metabisulfite, copper sulfate, lime) were added continuously, and the pH was controlled by automatic addition of lime suspension. Tests were carried out at room temperature. Samples of feed and treated effluent were taken at hourly intervals for process monitoring, and final samples were taken at steady state.

CombinOx® treatment tests performed on each feed pulp were conducted in continuous mode, in a properly agitated reactor(s) as described above, with continuous addition of regents. Samples of feed and treated effluent were taken at hourly intervals for process monitoring, and final samples were taken when the system reached steady state.

Caro's Acid tests were conducted batch-wise for the slurry solution samples at room temperature. Representative samples were taken for each test.

For the copper additions shown in **Tables 1 and 2**, an indexed value for copper was provided in parentheses below the actual Cu^{2+} addition, designated as “Fe +___ ppm”. Due to the fluctuations in the copper and especially the iron concentration in the feed, the indexed copper value was set up for comparison purposes and is equal to the theoretical amount of copper remaining after the feed and added copper are consumed by the precipitation of the iron cyanide as represented by the equation below:

$$Fe(CN)_6^{4-} + 2Cu^{2+} \rightarrow Cu_2Fe(CN)_6 \text{ (solid)}$$

This is based on the assumption that all the soluble iron in the feed is present as iron cyanide, and that all this iron cyanide reacts with the copper from the feed and the additional copper to form copper ferrocyanide.

6.2 Treatment Objectives

For all the effluent samples, a treatment target of 0.5 mg CN_{WAD} per liter of solution was set by the client. However, it was established that results as high as 1 ppm would be considered acceptable.

6.3 Treatment Results

6.3.1 SO_2/AIR Process

The SO_2/AIR cyanide destruction tests were performed on the slurry samples at 35% percent (wt%)solids. Results are summarized in **Table 1.**

Results at or below 1 mg CN_{WAD} /L were achieved in tests **SO_2/AIR #1, #3, #4 and #5**. The optimum conditions are shown in test **SO_2/AIR #1** where a 0.76 mg CN_{WAD} /L was achieved at pH 8.5 with a reagent addition of 6.0 g SO_2/g CN_{WAD} and some lime to maintain the pH. An 800 ppm Cu^{2+} addition was also used to catalyze the reaction and to precipitate the iron cyanide. This equates to an indexed copper value of 167 ppm Cu^{2+}. It may also be possible to use less copper as shown in test **SO_2/AIR #4**, with an indexed copper addition of 103 ppm. The 0.5 ppm CN_{WAD} treatment target was surpassed in **SO_2/AIR #5** using an extremely high copper addition.

6.3.2 CyPlus-CombinOx®

CombinOx® cyanide destruction tests were performed on the 35% solids slurry feed samples. Results are summarized in **Table 2**.

Results at or below 1 mg CN_{WAD} /L were achieved in tests **COMB #1 and #3.** The treatment target was exceeded in the optimized test, **COMB #3** with the addition of 4.51 g SO_2 & peroxygen per g CN_{WAD} , and some lime to maintain the pH at 9.0. A 1031 ppm Cu^{2+} addition was also used which equates to an indexed copper value of 75 ppm and required a retention time of 2 hours. The peroxide addition was unusually high.

6.3.3 Caro's Acid Process

Tests relating to Caro's Acid treatment of the 35% slurry were performed using batch treatment methods. Results are summarized in **Table 3.**

Due to site transport and temperature issues that dictated the use of more dilute reagents, the Caro's acid used for this report was generated under cooled conditions using 39% H_2SO_4 and 50% H_2O_2 with a 2:1 molar ratio of sulfuric acid to peroxide. The resulting Caro's acid solution had an exceptionally low conversion rate of peroxide to Caro's acid of just under 25%. Therefore, most of the oxidant was present as peroxide, which appeared to decompose on the iron compounds in the concentrate sample. Typically 70% peroxide and 93% sulfuric acid is used for generating Caro's acid solutions with conversion rates around 80% under cooled conditions.

Even when using a relatively high dose of Caro's acid solution in test **Caro's #5**, at 5.23 g 100% H2O2 and 30.2 g

H_2SO_4 / g CN_{WAD}, the resulting CN_{WAD} concentration was still above 20 ppm at 23.7 ppm.

7. DISCUSSION OF RESULTS

The SO_2/AIR and CombinOx® processes, appear to be effective in the removal of cyanide from the leach slurry, to reach levels of 1 mg CN_{WAD} / L or below. The Caro's acid process, however, could not reach levels below 20 mg CN_{WAD} / L, even when relatively large amounts of reagents were used. This is due in large part to the low reagent concentrations of peroxide and sulfuric acid, where a relatively small amount of the peroxide was converted to Caro's acid during the Caro's acid generation process.

Due to the fluctuations in iron and copper in the feed samples, an "indexed" copper addition was established to help compare the SO_2/AIR and CombinOx® processes. This is described in **Section 6.1**.

Referring to **Table 1**, the SO_2/AIR process worked effectively in test **SO_2/AIR #1** requiring 6 g SO_2 / g CN_{WAD} and an indexed copper addition of 167 ppm of Cu^{2+}(800 ppm actual). This produced a CN_{WAD} concentration of 0.76 ppm and a relatively low copper concentration of 0.07 ppm. Test **SO_2/AIR #4** produced an acceptable 1.01 ppm CN_{WAD} result using less SO_2 and copper on an indexed basis, at 5.5 g SO_2 / g CN_{WAD} and 103 ppm Cu^{2+}. However, the resulting copper and total cyanide values were much higher.

The CombinOx® tests, shown in **Table 2** also proved successful in producing acceptable results below 1 ppm CN_{WAD}. In test **COMB #3**, note the relatively low total cyanide and copper results.

8. OPERATING AND CAPITAL COST ESTIMATES

The laboratory test results and reagent unit cost data were used to provide operating cost estimates, based on the "typical" and "design" figures, for the various treatment options that were tested. A capital cost estimate is also provided based on the "design" conditions. These are summarized in **Tables 4 and 5**.

The operating costs in the tables are based on the reagent unit costs, labor and power costs provided by Miramar and CyPlus. The reagent costs are for delivery on-site.

The “typical” and “design” conditions, used for the operating and capital cost estimates in **Tables 4 and 5**, are shown below:

	Design	**Typical**
Tonnage: Concentrate Feed	67.2 dry tonnes/day	67.2 dry tonnes/day
Weight % Solids	40 %	45 %
CN_{WAD} Concentration	904 mg/L	697 mg/L
Copper	334	181
Iron	167	75
Availability	100%	90%

The information above was provided by Miramar. Note that there are some the differences from the testwork conditions.

9. CONCLUSIONS AND RECOMMENDATIONS

The conclusions and process recommendations given below are based on the laboratory results and operating cost estimates using unit costs and parameters outlined in Section 8 of the report. **NOTE: Changes to reagent unit costs can substantially change operating cost estimates and will impact on process selection.**

1. The testwork indicates that it was possible to treat the leached tails effluent sample to levels at or below of 1 mg CN_{WAD} /L, using SO_2/AIR and CombinOx® processes, as shown in **Tables 1 and 2**. It was not possible to achieve these low levels using Caro’s acid, shown in **Table 3**.

2. Based on the operating cost comparison in **Tables 4 and 5**, the SO_2/AIR process would appear to be the most economical in terms of the reagent costs alone, at $15.74 per tonne for “typical” conditions. CombinOx® was about 10% more expensive at $17.50 per tonne. The costs for electrical, manpower and maintenance have yet to be calculated.

3. The capital costs estimates for each process are shown at the bottom of **Tables 4 – 5** have yet to be determined.

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Table 1
SO_2/AIR Continuous Treatment Results

			SOLUTION ASSAYS						**REAGENT ADDITIONS**		
TEST	**STREAM**	**RET'N TIME (hours)**	**CN_{WAD} (ppm)**	**$^*CN_{TOT}$ (ppm)**	**Cu (ppm)**	**Ni (ppm)**	**Fe (ppm)**	**pH**	**SO_2 (g / g CN_{WAD})**	**$Ca(OH)_2$ (g /g CN_{WAD})**	**Cu^{2+} (ppm)**
	FEED		**631.7**	**1,510**	**81.60**	**1.99**	**314.3**	**10.5**			
SO_2/AIR #1 (Optimum)	C.I.L. Tails	2	0.76	1.85	0.07	0.13	0.39	8.5	6.0	2.05	800 **(Fe + 167 ppm)**
	FEED		**626.1**	**1,246**	**92.72**	**1.39**	**221.8**	**10.5**			
SO_2/AIR #2	C.I.L. Tails	2	51.30	161.7	55.30	1.287	39.50	8.6	5.0	2.24	25 **(Fe + 0 ppm)**
	FEED		**638.5**	**1,626**	**95.93**	**1.42**	**353.2**	**10.5**			
SO_2/AIR #3	C.I.L. Tails	2	0.87	0.87	5.29	1.11	<0.05	8.6	5.0	2.39	1100 **(Fe + 393 ppm)**
	FEED		**649.5**	**1,625**	**95.60**	**1.47**	**349.1**	**10.5**			
SO_2/AIR #4	C.I.L. Tails	2	1.01	6.87	10.20	1.29	2.10	8.5	5.5	2.80	800 **(Fe + 103 ppm)**
	FEED		**637.9**	**2,177**	**197.1**	**1.67**	**550.7**	**10.5**			
SO_2/AIR #5	C.I.L. Tails	2	<0.05	<0.10	0.17	0.15	<0.05	8.5	6.0	2.57	1500 **(Fe + 444 ppm)**

* Calculated Total Cyanide

Table 2
CombinOx® Continuous Treatment Results

			SOLUTION ASSAYS						REAGENT ADDITIONS		
TEST	**STREAM**	**RET'N TIME (hours)**	**CN_{WAD} (ppm)**	**$^*CN_{TOT}$ (ppm)**	**Cu (ppm)**	**Ni (ppm)**	**Fe (ppm)**	**pH**	**Total Peroxygen & SO_2 (g / g CN_{WAD})**	**$Ca(OH)_2$ (g /g CN_{WAD})**	**Cu^{2+} (ppm)**
	FEED		**641.5**	**1,517**	**183.9**	**1.61**	**313.5**	**10.5**			
Comb #1	C.I.L. Tails	2	0.94	1.58	5.02	0.49	0.23	9.0	3.10	0.89	1,000 **(Fe + 471 ppm)**
	FEED		**643.5**	**1,037.**	**96.8**	**1.80**	**140.8**	**10.5**			
Comb #2	C.I.L. Tails	2	19.80	46.35	8.72	0.36	9.5	9.0	3.10	0.86	346 **(Fe + 122 ppm)**
	FEED		**649.5**	**1,951**	**102.5**	**1.73**	**465.7**	**10.5**			
Comb #3 (Optimum)	C.I.L. Tails	2	0.22	1.75	0.14	0.45	0.55	9.0	4.51	1.04	1,031 **(Fe + 75 ppm)**
	FEED		**642.9**	**1,988**	**185.3**	**1.77**	**481.3**	**10.5**			
Comb #4	C.I.L. Tails	2	76.80	79.61	130.6	1.09	1.00	9.0	3.86	0.96	984 **(Fe + 75 ppm)**

* Calculated Total Cyanide

Table 3
Caro's Acid Batch Treatment Results

			SOLUTION ASSAYS						REAGENT ADDITIONS			
TEST	**STREAM**	**RET'N TIME (hours)**	**CN_{WAD} (ppm)**	**$^{*}CN_{TOT}$ (ppm)**	**Cu (ppm)**	**Ni (ppm)**	**Fe (ppm**	**pH**	**100% H_2O_2 (g / g CN_{WAD})**	**100% H_2SO_4 (g / g CN_{WAD})**	**$Ca(OH)_2$ (g / g CN_{WAD})**	**Cu^{2+} (ppm)**
	FEED		**631.50**	**1,511**	**72.30**	**1.66**	**313.5**	**10.5**				
Caro's #1	C.I.L. Tails	0.5	193.00	278.0	56.50	0.15	30.42	9.0	1.31 (1.0 X Stoich)	7.55 (2.0 X Stoich)	3.69	-
Caro's #2	C.I.L. Tails	0.5	71.50	157.0	47.10	0.12	30.58	9.1	2.62 (2.0 X Stoich)	15.1 (4.0 X Stoich)	7.56	-
Caro's #3	C.I.L. Tails	0.5	40.00	143.5	35.50	0.10	37.04	9.1	3.92 (3.0 X Stoich)	22.6 (6.0 X Stoich)	14.88	-
Caro's #4	C.I.L. Tails	0.5	28.50	129.2	29.65	0.09	36.04	9.0	4.57 (3.5 X Stoich)	26.4 (7.0 X Stoich)	22.19	-
Caro's #5	C.I.L. Tails	0.5	23.70	131.6	20.93	0.06	30.11	9.0	5.23 (4.0 X Stoich)	30.2 (8.0 X Stoich)	24.33	-

* Calculated Total Cyanide

APPENDIX A

Direct Colorimetric Determination of Cyanide With Picric Acid

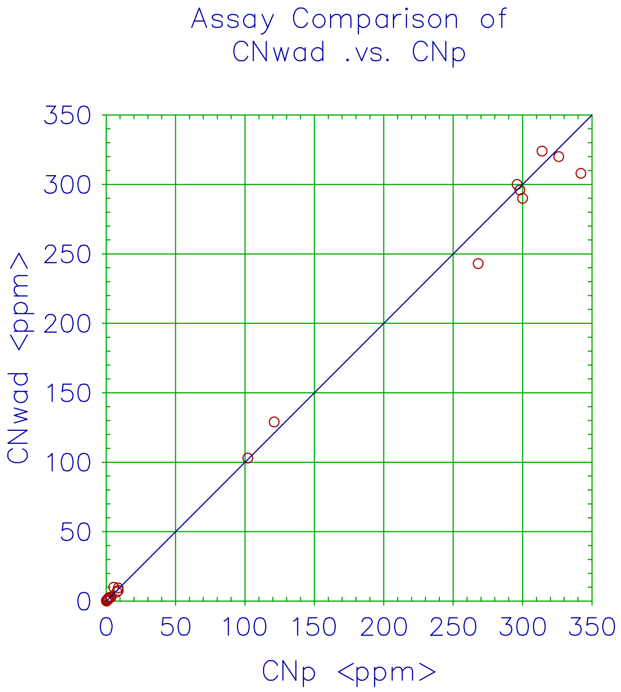
I Outline

Free cyanide and weak-acid dissociable cyanide reacts with the picric acid reagent to produce an orange colour, which can be measured colorimetrically at a wavelength of 520 nm. As with all colorimetric methods, standards must be prepared for comparison purposes.

The dissolved alkali metal picrate is converted by cyanide into the coloured salt of isopurpuric acid and its concentration is measured. For determination of cyanide below 0.1 ppm extractive preconcentration techniques can be used which are described in the original method. The presence of a small amount of nickel in the analyzed solutions has a positive effect on the overall performance of the method, but is not absolutely necessary.

II Application

The method is suitable for the determination of weak acid dissociable cyanide (CN_{WAD}) in effluents from flotation mills, gold cyanidation mills and electroplating shops. Since the detection limit for this procedure is 0.2 ppm CN_{WAD} it is especially useful for monitoring cyanide discharges to the environment. Below is a comparison of the results from the weak-acid dissociable cyanide distillation method (CN_{WAD}) and that obtained with the picric acid method (CN_P) described herein. It is apparent that CN_{WAD} is essentially the same as CN_P though it is useful to retain the distinction between the methods.



The reduction of picric acid is effected by free cyanide only. Cyanide tied up in copper, nickel, zinc or cadmium complexes is liberated by metathesis with:

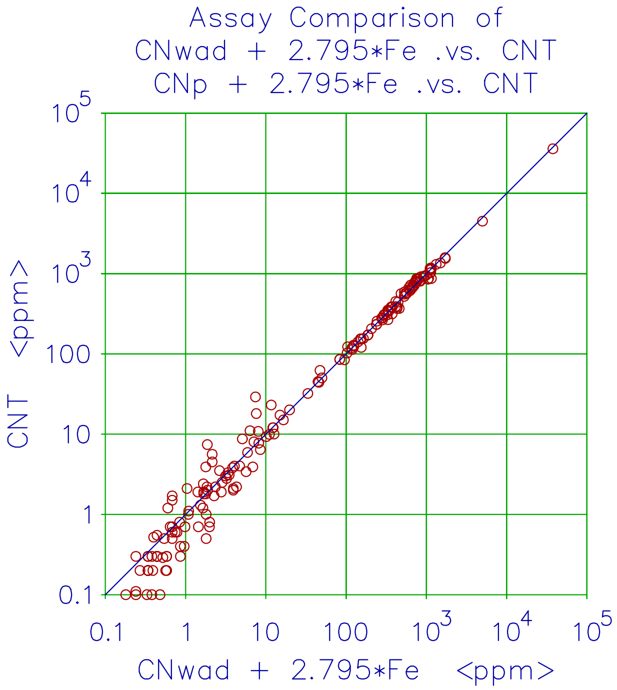
- diethylenetriaminepentaacetic acid (DTPA) or
- ethylenediaminetetraacetic acid (EDTA).

Iron-cyanide complexes, cobalt-cyanide complexes, gold-cyanide complexes, and silver-cyanide complexes do not react leaving their portion of cyanide undetermined. Usually only iron cyanide is present in any significant concentration so one can calculate total cyanide (CN_T) with one of the two formulae

$$CN_T = CN_P + 2.795 \text{ x Fe}$$

$$CN_T = CN_{WAD} + 2.795 \text{ x Fe}$$

As the concentrations of CN_P or CN_{WAD} and Fe approach zero, the formula becomes less exacting since a ligand other than cyanide might be present to keep the iron (Fe) in solution.



The direct colorimetric method allows for the accurate measurement of 10 - 200 µg CN^- in a sample aliquot of up to 50 mL. For samples containing greater than 1000 ppm CNp, dilute with distilled water. The table below should be used as a guide to determine the sample aliquot to be used for preparing the 100 ml mixture of the unknown.

Cyanide Concentration in Aliquot < ppm CN_P >	**Aliquot < mL >**
0.2 - 4	50
4 - 20	10
20 - 200	1
200 - 400	0.5
400 - 1000	0.2

III **Interferences**

Thiocyanate, cyanate and thiosulphate ions have no adverse effects and can be tolerated at levels normally occurring in gold mill effluents. Sulfide is a source of interference, 0.1 mg $S^{=}$ being equivalent to 0.025 mg CN^{-}. If present, sulfide ions can be readily removed by the addition of lead salts. However, it is unlikely that mill effluents would contain sulfide at levels large enough to significantly interfere in the cyanide determination. Sulfide particles which contact the picric acid reagent because of improper filtering of a gold bearing slurry, will also cause the $S^{=}$ interference.

The method requires a close control of pH since it affects the colour intensity produced by the cyanide-picric acid reaction. The most intense coloration results at pH 9.0 - 9.5. For maximum sensitivity and a good reproducibility of analytical results, the picric acid reagent solution should therefore be buffered. In the present procedure a mixture of sodium tetraborate and carbonate as well as DTPA itself serve this purpose. DTPA is preferred to EDTA due to more favourable values of acid ionization constants and stability constants of some metal chelates.

The method is highly recommended for monitoring the effluent of the Inco process since it is simple to do (once the picric acid reagent has been prepared) and any procedural errors will result in an assay biased high; whereas, any procedural errors in the distillation methods will bias the assay low. If the Inco Process has lost its catalytic activity, an orange colour may develop instantly upon addition of the picric acid reagent due to an $SO_3^{=}$ interference (unoxidized SO_2 in solution). The interference can be removed by adding $CaCl_2$ which will precipitate the $SO_3^{=}$ as $CaSO_3$. The precipitate must be filtered out prior to using the colorimeter. If the $SO_3^{=}$ is not precipitated out of solution the final result may be biased high.

IV Safety Precautions

Solutions of picric acid (trinitrophenol) are safe in ordinary laboratory use. However, in dry form the acid and especially some of its salts have explosive properties. This requires that all picric acid solutions be thoroughly washed down with water. Spills must be carefully wiped up. Picric acid has the tendency of staining the skin, and wearing protective hand gloves is therefore recommended. Glass stained by picric acid is best washed with methanol or acetone.

V Direct Colorimetry (10 - 200 μg CN^-)

Measure the absorbency of solutions more deeply coloured than the reagent blank at 520 nm using the reagent blank as the reference (Note 3).

VI Calibration and Sample Analysis

For the most accurate results, add only a portion of the distilled water (75 mL) called for in preparing the standards and unknowns. After the colour has been developed, add the contents to a 100 mL volumetric flask and wash out the conical flask with distilled water and add it to the volumetric flask until the 100 mL mark has been reached. Always measure absorbency against the respective reagent blank. Plot the absorbency readings vs. μg CN^- added in the aliquots of the standard cyanide solution, to construct the calibration graph. The plot should be a smooth gentle curve.

VII Calculation

Convert the absorbency reading of the aqueous solution or the extract into micrograms of cyanide using the calibration graph. If you are using the colorimeter in direct reading mode your reading is already in micrograms of cyanide and no graph is needed. The graphical method is by far the most accurate of the two and less prone to error. The colorimeter in direct reading mode uses a single point calibration and generates a linear response to absorbency changes whereas the actual response for a range of colour standards falls on a typical Beer's Law curve. By using the graphical method this linearization error can be avoided as well as the possible error due to the calibration of the colorimeter with older, contaminated standards.

Once the microgram of cyanide is known calculate the cyanide concentration in the original sample solution as follows :

$$ppm\ CN_P = \frac{mg\,CN^-}{L} = \frac{\mu g\ CN^-\ from\ the\ Calibration\ Graph}{Aliquot\ Volume\ in\ mLs}$$

VIII **Notes**

1. A white precipitate of calcium carbonate might separate from samples containing large quantities of calcium. This is dissolved by addition of 0.1-0.2 g of EDTA disodium salt.

2. When heating the picric solutions they should reach a temperature close to the boiling point but should not be allowed to boil for any length of time. Alternately, the analysis is carried out in 150 mL conical flasks, which are then immersed in a boiling water bath for a period of 30 minutes.

3. The absorbency of the reagent blank usually varies between 0.006 - 0.009 (520 nm, slit width 0.03 mm, 1-cm glass cell). By using the standard, which is darker than the sample the result will be biased slightly high. The converse is also true.

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