

## **ANALYTICAL - CYANIDE BY PICRIC ACID**

### **Introduction To Picric Acid Method :**

The picric acid method is used by the operators to monitor the cyanide concentrations in the feed and in the effluent. By having the operators perform these routine analysis they will be able to monitor the CN Load (needed for the SO<sub>2</sub> dosage) and the CN effluent (needed to optimize the operation of the Inco reactor).

The assay laboratory may also use the picric acid method since it is much less time consuming than conventional distillation methods and generally give assays that are either equal or slightly higher than a weak-acid dissociable distillation.

No other cyanide assaying method is as easy to perform when trying to measure cyanide concentrations of less than 1.0 ppm CN<sub>WAD</sub>. The operators use the picric method to obtain a rough estimate of the cyanide concentration for control purposes; though they, or the laboratory, can obtain over two significant digits by exercising more care and by using a colorimeter.

The applicability of the picric acid method for cyanide determinations is discussed on the following pages under the title "laboratory procedure". The laboratory procedure sub-section contains all information needed to perform the picric acid determination for Cyanide. Preparation of the various picric solutions and coloured standards are located on separate sheets to allow for copying for ready reference by laboratory personnel.

The "mill picric" is made of fully strength "buffered picric acid reagent" with the required dilution water all ready added. This simplifies the procedure when the operators are instructed to control the cyanide concentrations above 5 ppm CN<sub>WAD</sub>.

The procedures used by the operators are also included in this section of the manual for reference by laboratory personnel. These procedures are also found in the "operating procedure" section of this manual for use by the operators.

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## ANALYTICAL - CYANIDE BY PICRIC ACID

### Laboratory Procedure

#### 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 520 nm or can be estimated by eye. As with all colorimetric methods, standards must be prepared for comparison purposes.

Chemically speaking, 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 0.26 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.

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### Laboratory Procedure (cont'd)

#### III Interferences

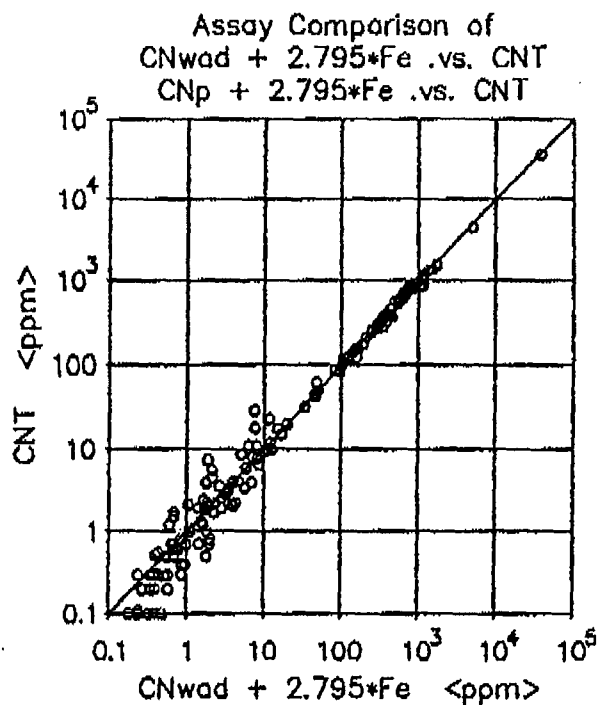
Thiocyanate, cyanate and thiosulfate ions have no adverse effects and can be tolerated at levels normally occurring in gold mill effluents. Sulfide is a source of interference, 0.1 mg  $S^{2-}$  being equivalent to 0.025 mg  $CN^-$ . If present, sulfide ions can be readily removed by the addition of 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  $S^{2-}$  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 favorable 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  $SO_3^{2-}$  interference (unoxidized  $SO_2$  in solution). The interference can be removed by adding  $CaCl_2$  which will precipitate the  $SO_3^{2-}$  as  $CaSO_3$ . The precipitate must be filtered out prior to using the colorimeter. If the  $SO_3^{2-}$  is not precipitated out of solution the final result may be biased slightly high.

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### Laboratory Procedure (Continued) :



The direct colorimetric method allows for the accurate measurement of 8 - 160  $\mu$ g CN<sup>-</sup> in a sample aliquot of up to 10 mL. For samples containing greater than 800 ppm CN<sub>p</sub>, dilute with distilled water. The table below should be used as a guide to determine the sample aliquot to be used for preparing the 40 ml mixture of the unknown.

Cyanide Concentration in Aliquot < ppm CN <sub>p</sub> >			Aliquot < mL >
0.2	-	16	10
2	-	32	5
10	-	160	1
20	-	320	0.5
50	-	800	0.2

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### **Reagent Preparation**

The following is the recipe for preparing "Buffered Picric Acid Reagent".

- 1) Dissolve 40 g DTPA and 16 g NaOH in approximately 600 mL of distilled water using a magnetic stirrer.
- 2) Add 6 g of moist picric acid (10% to 15% moisture content). If the moisture content is 25% to 50%, drain excess water then weigh 7 g of the reagent.
- 3) In a separate beaker, add 300 mL distilled water and either 14 g  $\text{Na}_2\text{B}_4\text{O}_7$  or 27 g  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and warm until dissolved and add it to the 600 ml in step 1.
- 4) Add 8 g  $\text{Na}_2\text{CO}_3$  and stir until all is dissolved.
- 5) Cool to room temperature and filter through 0.45  $\mu\text{m}$  paper (if necessary).
- 6) Add distilled water to obtain 1 litre total volume and then mix well.

### **Mill Picric Acid Recipes**

The operators monitor the cyanide in the effluent using a simplified version of the laboratory procedure. In the simplified version, the operator measures a fixed volume of filtered effluent (10 mL), adds a fixed volume of "mill picric" (30 mL) and then "cooks" it to develop the colour. "Mill Picric" is simply "Lab Picric" that has been diluted with water 1:2. The coloured standards are labelled such that no major calculations are required to evaluate a sample. In order to measure more than 16 ppm cyanide, dilution is required per the laboratory method. "Mill Picric" can still be used but the sample plus dilution water must total 10 mL.

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### **Laboratory Procedure (cont'd)**

#### **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 a sink 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 (8 - 160 $\mu\text{g CN}^-$ )**

Measure the absorbance 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**

The following pages are self-contained analytical sections that describe the various tests needed to operate the Inco System effectively. They are located on separate pages so that they may be copied and posted for easy reference. The pages in order of appearance are:

- Buffered Picric Acid Reagent
- Mill Picric Acid Recipes
- Standard Preparation (Using NaCN)
- Alternate Sample Heating Using a Microwave
- Colorimeter Calibration
- Colorimeter Standardization and Sample Reading
- Effluent Monitoring - Standard Operator Method
- Feed Monitoring Using Silver Nitrate Titrations
- Feed Monitoring Using Picric Acid - Standard Operator Method
- Base Metals by AA

For the most accurate results, add only a portion of the distilled water 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 mark has been reached. Always measure absorbance against the respective reagent blank. Plot the absorbance readings vs.  $\mu\text{g CN}^-$  added in the aliquots of the standard cyanide solution, to construct the calibration graph. The plot should be a smooth curve.

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### Preparation of Standards :

#### Sodium Cyanide Stock Standards

- 1000 ppm CN: Dissolve 1.885 NaCN and 1 gram NaOH in distilled water and dilute to 1 litre in a volumetric flask. This is equivalent to 1 mg CN/mL (1000 µgCN/mL or 1000 ppm CN).
- 10 ppm CN: Take 10 mLs of the 1000 ppm CN standard and dilute this to 1 litre in a volumetric flask to yield a 10µgCN/mL stock-solution.

#### Laboratory Working Standards for Calibration

Take six (6) 250 mL erlenmeyer flasks and add 10 mL of buffered picric acid reagent to each. Then add the cyanide solution and distilled water as given below. Heat as instructed on the following pages (either on a hot plate or in a microwave). Other standards can be generated but are not required for general operation of the Inco Process.

Blank:	Add 30 mL distilled water.
20 µgCN:	Add 2 mL of 10 ppm stock and 28 mL of distilled water.
40 µgCN:	Add 4 mL of 10 ppm stock and 26 mL of distilled water.
80 µgCN:	Add 8 mL of 10 ppm stock and 22 mL of distilled water.
120 µgCN:	Add 12 mL of 10 ppm stock and 18 mL of distilled water.
160 µgCN:	Add 16 mL of 15 ppm stock and 14 mL of distilled water.
250 µgCN:	Add 25 mL of 10 ppm stock and 5 mL of distilled water.

**ANALYTICAL - CYANIDE BY PICRIC ACID****Mill Picric Acid Recipes (Continued)**

Recipe Code	A	B	C	D
Useful Cyanide Range	0-5 ppm	0-16 ppm	0-320 ppm	0-800 ppm
Volume Buffered Picric Acid	1 L	1 L	1 L	1 L
Volume Distilled Water	0	2 L	2 L	2 L
Volume Mill Picric Prepared	1 L	3 L	3 L	3 L
Sample Volume Used	30 mL	10 mL	0.5 mL	0.2 mL
Volume Mill Picric	10 mL	30 mL	30 mL	30 mL
Volume Water	0 mL	0 mL	9.5 mL	9.8 mL
Total Volume Cooked	40 mL	40 mL	40 mL	40 mL
160 $\mu\text{gCN}^-$ standard reads:	5.3 ppm	16 ppm	320 ppm	800 ppm
120 $\mu\text{gCN}^-$ standard reads:	4 ppm	12 ppm	240 ppm	600 ppm
80 $\mu\text{gCN}^-$ standard reads:	2.7 ppm	8 ppm	160 ppm	400 ppm
40 $\mu\text{gCN}^-$ standard reads:	1.3 ppm	4 ppm	80 ppm	200 ppm
20 $\mu\text{gCN}^-$ standard reads:	0.6 ppm	2 ppm	40 ppm	100 ppm
0 $\mu\text{gCN}^-$ standard (blank) reads:	0 ppm	0 ppm	0 ppm	0 ppm

1. The standards and samples should be of the same volume when cooked and should be in the same size erlenmeyer flask.
2. The  $\mu\text{gCN}^-$  divided by the mLs of aliquot gives ppm.



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### **Heating A Picric Sample in A Microwave Oven :**

A microwave oven can be used minimize the time requirement for colour development. This approach is often used when the picric acid method is used for monitoring cyanide in the effluent by the operators and is not recommended for analytical use. Gloves must be worn by the operator when handling hot picric solutions when the microwave is used.

Any spills must be thoroughly cleaned immediately before operating the microwave again. This prevents formation of dry picric acid salts which are potentially explosive.

Heating time depends on type and power output of the microwave oven. Sample colour development should be monitored closely by the operator.

The following procedure will allow safe and quick colour development.

- 1) Place sample in the centre of the microwave.
- 2) Set heating time for 2 minutes, close the door and begin heating. The power level should be on "High".
- 3) Heat for 22 seconds open the microwave door and swirl the sample carefully. The sample should be fairly warm. The swirling prevents hot spots from forming in the solution that would cause bumping and possibly an eruption of the sample.
- 4) Close the door and heat the solution to the first sign of boiling and then immediately stop the heating. With caution and using hand protection (solution is hot), swirl the flask to homogenize the solution.
- 5) Place the flask back into the oven and heat for a further 5 to 20 seconds until the solution just starts to reboil.
- 6) Turn the microwave oven off, carefully remove the sample solution from the oven and allow it to sit for 4 to 5 minutes before cooling the flask in a water bath.
- 7) The resulting colour can be compared to the labelled standards immediately to obtain an approximate result. Since hot samples are darker, the assay is higher by 50% than the true value. For accuracy, cool the sample to room temperature and measure with the colorimeter.

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### Preparation of Standards : (Continued)

#### Heating Instructions

Once the standards have been mixed, the colour is developed by heating. For the colorimetric standards, heat on a hot plate for 30 minutes (not less) near to boiling.

The standards must be cooled to room temperature before they can be used. A water bath is commonly used. Unknowns must be at the same temperature as the standards for best results since the colour intensity increases with temperature.

Alternately the standards may be prepared by the microwave heating method described further on in this section.

**ANALYTICAL - CYANIDE BY PICRIC ACID****Colorimeter Set-Up :**

Whenever the colorimeter is shut off it must allowed to warm up warm-up for 5 minutes prior to calibration and use.

- Check that the slide in filter is in the filter block (6). Never turn colorimeter on if filter is missing.
- Ensure that the fiber optics (8) and "pen" are securely attached to the unit (7). The two retaining screws should be only hand tight (5).
- Turn function selector (2) to "Abs".

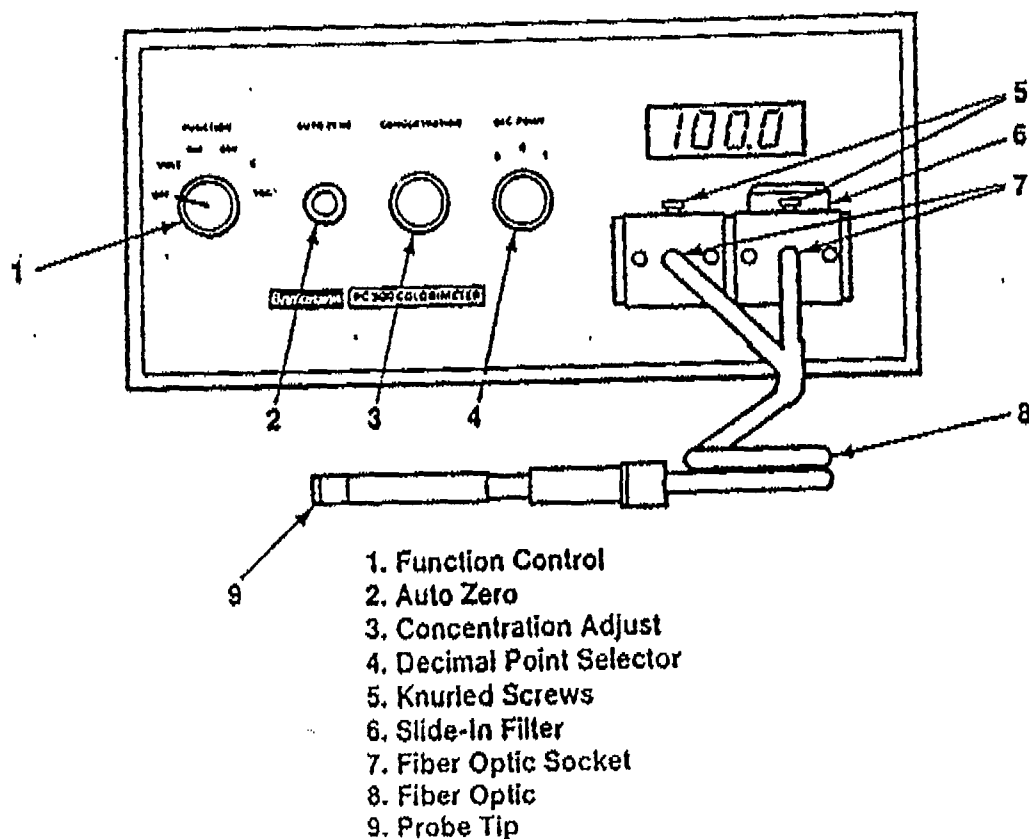
## ANALYTICAL - CYANIDE BY PICRIC ACID

### Colorimeter

The diagram below shows the front view of the Brinkmann PC 900 colorimeter;

### PROBE COLORIMETER PC 900

FRONT



The Brinkmann PC 900 Colorimeter, can be used in conjunction with the Picric Acid Test to give a very accurate CN<sup>-</sup> determinations. The colorimeter requires a 5 minute warm-up period to provide maximum stability of operation, therefore it is best to turn it on at the start of any set of sample determinations, even before the samples are filtered.

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#### **Effluent Monitoring Using Picric Acid (by Operators) :**

- 1) Sample the effluent leaving the Inco Reactor at the either the tailings pump box or from the top of reactor.
- 2) Filter solution by gravity.
- 3) Take 10 mLs of the filtrate and pour it into a clean 125 mL flask. Label the flask with an R1 for reactor #1 or an R2 for reactor #2.
- 4) Add 30 mLs of mill picric acid reagent to the 125 mLs flask and swirl the solution for mixing.
- 5) Cover the flask with a cork or plastic cap to reduce evaporation. Place into a microwave and heat for about 22 seconds or until the solution just begins to boil. Remove the flask from the microwave (caution HOT) and swirl contents to mix. Place flask back into microwave and bring to a boil a second time. Remove the sample from the microwave and allow to stand for 4 to 5 minutes to complete the colour development. See Heating Picric Sample in a Microwave Oven for a more detailed description of this step.
- 6) Cool the sample. (Note : sample may be compared to the standards while hot but the cyanide will be appear to be about 50% higher than when it has cooled.)
- 7) Match the colour of the sample with one of the coloured standards. The " $\mu\text{g}$ " number labelled on that standard divided by the number of mls of the sample aliquote is the ppm  $\text{CN}_p$  in the treated effluent.

If the colour of the sample is significantly lighter or darker than the colour of the "target colour standard", the process is in need of some fine tuning. If the colour is close to that of the target effluent standard the process is running fine. The supervisor should be contacted for advice if one is unable to find the problem related to unacceptably high cyanide levels in the effluent.

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### Using a Colorimeter to Obtain a Cyanide Assay :

Once the colorimeter has been warmed up, very accurate cyanide assays can be obtained. The colorimeter is zeroed and calibrated prior to reading the unknown sample using the following steps :

- Place tip of the pen into blank solution while in %Abs mode and press the "ZERO" button on the instrument. Never zero colorimeter in the concentration mode. The function switch is set back to absorbance and zeroed, then turned back to concentration.
- Turn knob (2) to concentration (c). The display should still read zero. (zero absorbance = zero concentration).
- Remove tip of the pen from the blank, rinse in water and dry the outside of the pen with tissue. (Be careful not to touch the optics of the pen tip.) This should prevent excessive standard cross contamination or dilution.
- Choose standard that is closest in colour to the sample that requires reading. If the sample is mid-way between two standards choose the high standard.
- Place pen tip into solution and adjust concentration knob (3) until display reads the value of the chosen standard (eg. 40  $\mu\text{gCN}$  standard set conc. to 40).
- The sample must be cooled to room temperature before attempting the next step.
- Remove pen tip from standard and insert the pen into sample solution. The display will read  $\mu\text{gCN}$ . Note that no drying is necessary when reading the sample.
- Divide the  $\mu\text{g CN}^-$  by the aliquot volume in mLs to obtain the  $\text{CN}^-$  concentration in ppm.
- Return the probe to a beaker of fresh distilled water and turn off the instrument if not in use.