DIRECT SPECTROPHOTOMETRIC METHOD USING PICRIC ACID REAGENT

I. Outline

Free cyanide and weak-dissociable cyanide reacts with picric acid in solution to produce a bright orange colour which can be measured using a spectrophotometer at 520 nm. The dissolved alkali metal picrate is converted by cyanide into the coloured salt of isopurpuric acid and its concentration is measured. The presence of a small amount of nickel in analysed solutions has a positive effect on the overall performance of the method. The detection limit of this procedure is 0.26 mg/L. The method is suitable for the determination of weak acid dissociable cyanide. The reduction of picric acid is effected by free cyanide only. Cyanide that is complexed with copper, nickel, zinc or cadmium complexes can be 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 complexed cyanide in tact.

The direct spectrophotometric method allows for the measurement of 20-300 µg cyanide in a sample aliquot of up to 75 mL. Samples containing greater than 600 µg cyanide need to be diluted.

II. 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 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 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.

III. 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.

IV. Reagents

Buffered Picric Acid Reagent

Dissolve 40g of diethylenetriaminepentaacetic acid and 16 g of NaOH in 900-950 mL of water. Next dissolve, in the order given, 6 g of picric acid, 14 g of anhydrous sodium tetraborate or 27 g $Na_2B_4O_7.10H_2O$ and 8 g of anhydrous sodium carbonate. The pH of this solution is 8.7, and would increase to 9.0 on a four-fold dilution. After reacting with cyanide the solution's final pH should be 9.2-9.3.

Nickel Solution, approximately 100 mg/L Ni.

Dissolve 0.22 g of $NiSO_4.6H_2O$ and 1 g of NaCl in 500 mL of water.

Standard cyanide solution, 1000 mg/L cyanide

Dissolve 2.503 g of KCN and 1 g of KOH or NaOH in water and dilute to 1 litre. Make further dilutions as necessary for the preparation of the calibrating working standard.

V. Procedure

Transfer into a 150 mL beaker a suitable volume of samples solution which contains 1-300 µg of cyanide. Add 1 mL of nickel solution, swirl, and dilute with water to about 70 mL. Measure about 70 mL of water in another beaker, add 1 mL of nickel solution and carry through the procedure as the reagent blank. Add 25.0 mL of buffered picric acid reagent to each beaker and heat for 35 minutes on a hotplate with surface temperature adjusted to 160 ^{0}C, without allowing to boil. If a white precipitate of calcium carbonate forms add 0.1-0.2 g of EDTA disodium salt. Cool the solutions to room temperature, transfer to 100 mL volumetric flasks and dilute to volume.

Measure the absorbance of the solutions more deeply coloured than the reagent blank at 520 nm using the reagent blank as the reference. The absorbance of the reagent blank usually varies between 0.006 – 0.009 (520 nm, slit width 0.03 mm, 1 cm path cell).

VI. Calibration

Into 150 mL beakers pipette aliquots of the standard cyanide solution containing 25, 50, 100, 200 and 300 µg cyanide. Add 1 mL nickel solution to each of them, mix, and dilute to about 70 mL with water. Add 25.0 mL of buffered picric acid reagent and proceed as described under "procedure". Always measure absorbance against the respective reagent blank.

Plot the absorbance readings vs. µg cyanide added in the aliquots of the standard cyanide solution, and construct the calibration graph.

VII. Calculation

Convert the absorbance reading of the aqueous solution or the extract into micrograms of cyanide using the calibration graph. Calculate the cyanide concentration in the original samples solution as follows:

mg/L CN⁻ = A/B where : A = µg CN⁻ found from the graph and B = volume, in mL, of the sample solution used for the analysis.

VIII. Reference

Iamarino, P.F. (1989) The direct spectrophotometric determination of cyanide with picric acid reagent. JRGRL June 1 1989. INCO Ltd. (based on V.J.Zatka method (JRGRL, November 1980 which was a modification of the method of D.J. Barkley and J.C. Ingles, Report 221, CANMET, (February 1970).