# The Picric Acid Method for Determining Weak Acid Dissociable (WAD) Cyanide

## 1.0 Introduction

Picric acid can be used in a colorimetric procedure to determine the concentration of weak acid dissociable (WAD) cyanide. In the presence of free cyanide, picric acid is reduced to the coloured isopurpuric acid, with the colour intensity directly proportional to the concentration of free cyanide originally present in the sample. In this procedure, cyanide that is weakly complexed with metals such as cadmium, copper, nickel and zinc is first dissociated by the addition of a chemical ligand, and the resulting free cyanide is then able to react with picric acid. Cyanide bound with iron or cobalt is not measured with this method.

## 2.0 Equipment

1. Visible range spectrophotometer for reading absorbance at 520 nm.
2. Heated water bath.
3. pH meter.
4. Balance.
5. Beakers, pipettes and volumetric flasks.

## 3.0 Safety Precautions

Solutions of picric acid, also known as trinitrophenol, are safe for ordinary laboratory use. However, in dry form picric acid and some of its salts have explosive properties. This requires that all solutions of waste picric acid be thoroughly washed down a sink with water. Spills must be carefully cleaned to prevent drying.

Picric acid will stain the skin, therefore the use of gloves is recommended.

## 4.0 Interferences

Thiocyanate, cyanate and thiosulphate to not affect the method at levels normally encountered in samples. Sulphide imparts a positive interference on results, so samples should be pre-screened for the presence of sulphide. This can be done using lead carbonate or lead acetate, which forms a dark colour in the presence of sulphide due to the formation of insoluble lead sulphide. If sulphide is present, lead carbonate or lead acetate should be added in a quantity sufficient to removal sulphide. Treated samples should be filtered after treatment with lead carbonate or lead acetate to remove precipitates.

## 5.0 Limitations

The method requires close control of sample pH since the intensity of colour development varies outside of the pH range of 9.0 to 9.5. Buffer solutions are prepared to provide a sample pH in this range, but samples used with the spectrophotometer should periodically be checked to ensure the pH is within this range.

The method provides reliable results for WAD cyanide concentrations above about 0.50 mg/L.

## 6.0 Reagents

6.1 Nickel Solution

- Dissolve 0.22 grams of nickel sulphate ($NiSO_4$-$6H_2O$) into 100 mL of deionised water.
- Add 1.00 gram of sodium chloride (NaCl) and dilute to 500 mL.

6.2 Picric Acid Solution

- Dissolved 40 grams of diethylenetriaminepentaacetic acid (DTPA) into 800 mL of deionised water.
- Dissolve 16 grams of sodium hydroxide (NaOH) in 50 mL of deionised water; add 20 mL of this solution to the DTPA solution. Save the remaining 30 mL.
- Add 6 grams of picric acid to the DTPA solution.
- Add 14 grams of sodium borate ($Na_2B_4O_7$ anhydrous) to the DTPA solution.
- Add 8 grams of sodium carbonate ($Na_2CO_3$ anhydrous) to the DTPA solution.
- Adjust the pH of the DTPA solution to 8.7 using the remaining NaOH solution.
- Dilute the DTPA solution to 1 litre using deionised water.

6.3 Sodium Cyanide Solution

- Dissolve 2 grams of sodium hydroxide (NaOH) into 50 mL of deionised water.
- Add 0.189 grams of sodium cyanide (NaCN) and dilute to 100 mL using deionised water.

## 7.0 Calibration

1. Pipette 10 mL of the sodium cyanide solution into a 100 mL volumetric flask.

2. Add 2 grams of sodium hydroxide (NaOH) to the volumetric flask and dilute to 100 mL using deionised water.

3. Into five separate 100 mL volumetric flasks, pipette 0.25 mL, 0.50 mL, 1.00 mL, 2.00 mL and 3.00 mL of the diluted sodium cyanide solution. Dilute each flask to 100 mL using deionised water. These dilutions correspond to cyanide (CN) masses of 0.025, 0.050, 0.100, 0.200 and 0.300 milligrams.

4. Measure the absorbance of these five dilutions of sodium cyanide according to the procedure in Section 9.0. Also run a deionised water blank sample.

5. Prepare a curve of absorbance versus milligrams of cyanide (CN).

## 8.0 Sample Preparation

Filter the sample if suspended solids are present that may interfere with spectrophotometer readings.

## 9.0 Procedure

1. Pipette 10 mL of the sample into a 100 mL volumetric flask.
2. Add 1 mL of the nickel solution.
3. Add 30 mL of deionised water.
4. Add 25 mL of the picric acid solution.
5. Heat volumetric flask in a boiling water bath for 20 minutes.
6. Remove volumetric flask from boiling water bath and cool to room temperature.
7. Dilute contents of volumetric flask to 100 mL using deionised water.
8. Measure the absorbance of the solution at 520 nm using deionised water as a blank reference.
9. If the absorbance falls outside of the calibration graph prepared in Section 8.0, repeat analysis with a smaller volume of sample in Step 1 of this procedure.

## 10.0 Calculation

The WAD cyanide concentration of the sample is determined using:

$$CN_{WAD}\ (mg/L\ CN) = \frac{(mg\ of\ CN\ from\ calibration\ curve)}{(mL\ of\ sample)} \times 1{,}000$$

For most samples, the total cyanide concentration can be calculated using:

$$CN_{TOTAL}\ (mg/L\ CN) = CN_{WAD} + 2.8 \times Fe\ (mg/L)$$