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Spectrophotometric Determination of Cyanide in Passaic River Paterson New Jersey by Distillation and Colorimetric Method with Pyridine: Barbituric Acid Reagent

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Abstract

Purpose: This work determines the concentration of total cyanide in the Passaic River in the New Jersey Area.

Methodology: The concentration of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-barbituric acid to form a stable complex. Therefore, before chlorination of cyanide, all cyanide compounds present in sample must be broken down by an acid reflux and distillation.

Findings: The cyanide concentration in the Passaic River sediment solution and non-running wastewater was determined by measuring absorbance at max 578 nm, and cyanide amount has been found less than 0.005 ppm under the NEPA permit compliance. Industrial facilities who discharge wastewater to public waterways in the United States, stringent limits on cyanide, typically with monthly average effluent limits set around 0.005 ppm or less.

Unique contributor to theory, policy and practice: This method is applicable to the determination of cyanide in drinking, saline, groundwater, surface water as well as domestic and industrial wastewater.

Keywords: *Cyanide, Spectrophotometric Determination, Distillation, Pyridine- Barbituric Acid*

1. INTRODUCTION

Cyanide is an extremely toxic waste product of many industrial process such as electroplating, case hardening of steel, ore refining, and scrubbing of stack gases from blast and producer gas furnaces. Natural waters do not contain cyanide. Its presence normally indicates contamination from an industrial source.

The National Toxics Rule (NTR) established a cyanide (CN) freshwater aquatic life chronic criterion of 5.2 µg/L [1]. Cyanide does not accumulate in the body and does not cause chronic disease but because of its ability to bind iron in blood by forming complexes, it can inhibit oxygen transfer to the cells [2].

All drinking water, both tap and bottled, include surface sources such as rivers, stream lakes, and reservoirs, and ground water source (wells) may contain small amounts of some contaminants [3] . EPA has taken a large role in performing ongoing water analysis.

The **Passaic River** is a river, approximately 80 miles (130 km) long,[4] in Northern New Jersey. The river in its upper course flows in a highly circuitous route, meandering through the swamp lowlands between the ridge hills of rural and suburban northern New Jersey, called the Great Swamp, draining much of the northern portion of the state through its tributaries.

The Passaic River's lower reach is a 17-mile tidal stretch from Dundee Dam in Clifton, NJ, to Newark Bay. The Lower Passaic has borne a heavy burden of pollution from a century of industrialization in the Passaic River Watershed.

The Passaic River system's drainage basin covers approximately 2,400 km^2, (935 sq mi) of northern New Jersey, and Rockland and Orange counties in southern New York. The river system is characterized by a complex web of major and minor tributaries, draining much or part of eight New Jersey counties (about 10% of the state). After flowing due south for several miles, the river turns east at Harrison, makes an S-curve, then turns south, and unites with the Hackensack River as it completes the journey to Newark Bay. In its lower (southern) portion, it flows through the most urbanized and industrialized areas of the state, including along Downtown Newark. The lower river suffered from severe pollution and industrial abandonment in the 20th century. In April 2014, the U.S. Environmental Protection Agency (EPA) announced a $1.7 billion plan to remove 4.3 million cubic yards (3.3×10^6 m^3) of toxic mud from the bottom of lower eight miles (13 km) of the river. It is considered one of the most polluted stretches of water in the nation, and the project is one of the largest toxic cleanups ever undertaken in the nation.[5]

SCOPE AND APPLICATION

Standard operating Procedure for the analysis of cyanide in water is based on Method

4500CN^- C, E from "Standard Methods for the Examination of Water and Wastewater" 22nd Edition (2012).

This method is applicable to the determination of cyanide in drinking, saline, groundwater, surface water as well as domestic and industrial wastewater.

The colorimetric procedure is used for concentrations in the range of 0.005 mg/L to 1.0 mg/L

2.0 SUMMARY OF METHOD

Hydrogen cyanide (HCN) is liberated from an acidified sample by distillation and purging with air. The HCN gas is collected by passing it through a NaOH scrubbing solution. The cyanide concentration in the scrubbing solution is determined colorimetrically by reaction with chloramine–T at a pH less than 8 without hydrolyzing it to cyanate. After the reaction is complete cyanogen chloride (CNCl) is formed which upon addition of a pyridine- barbituric acid reagent yields a red-blue color. Maximum color absorbance in aqueous solution is between 525 and 582 nm. To obtain colors of comparable intensity use the same salt content in sample and standards.

3.0 INTERFERENCES

Interferences are eliminated or reduced to a minimum by the distillation process that is part of the procedure.

Sulfide ions must be removed prior to distillation by the addition of lead acetate. Sulfides adversely affect the colorimetric and titration procedures. To determine how much to add, use a lead acetate test paper. Use lead acetate test paper that is saturated with acetate buffer solution. Keep adding lead acetate dropwise until when checked on the test paper, no dark color is formed. Powdered lead carbonate, instead of lead acetate solution, can also be used to remove sulfide interference if the sample concentration is high. Using the powdered lead carbonate will avoid significantly lowering the pH.

The sample is preserved upon collection with sodium hydroxide only, to insure a pH of 12 or greater. Upon arrival of the sample at the lab check the presence of oxidizing agent (such as chlorine) with test paper of saturated KI plus starch and pH 4.0 acetate solution (keep these papers in a closed vial under inert atmosphere). If the paper turns blue an oxidizing agent is present. To a 500 mL sample add 2.0 gm sulfamic acid and 0.1 gm ascorbic acid.

If the sample contains noticeable concentration of fatty acids remove by extraction with hexane prior to the distillation.

Hexane extraction procedure:

Acidify 200 ml of sample with 1:10 acetic acid to a pH between 6.0 and 7.0 in a fume hood as quickly as possible.

Immediately after adjusting the pH, extract the sample using 40 ml of hexane in a separatory funnel.

After extraction immediately raise the pH of the aqueous layer to a pH >12 with NaOH solution. Discard the organic layer.

High carbonate concentrations which may produce excessive CO_2 gas (leading to foaming) can be removed by preserving the sample with calcium hydroxide- $Ca(OH)_2$ instead of NaOH. To preserve sample with $Ca(OH)_2$ slowly add $Ca(OH)_2$ with stirring to pH 12-12.5. After precipitate settles, decant supernatant liquid for analysis.

4.0 SAMPLE HANDLING AND PRESERVATION

Collect 500 mL several samples every 1 mile of Passaic River in a glass or plastic containers that contain sodium hydroxide pellets. All bottles must be thoroughly cleaned and rinsed with reagent water. Mixed very well and make them 1L sample. Cool the sample to ≤4°C upon transfer to lab. Check for interferences upon arrival at the lab and treat as stated in Section 3.0

Holding time (in a refrigerator) is 14 days [6].

5.0 APPARATUS

Hach 3000DR Spectrophotometer with 5 cm cell (holds 25 mL of solution) for use at 578nm providing a light path of 10 mm or 25 mm, or BioSpech -1601 Spectrophotometer Shimadzu/Envro Midi Dist Enviro MIDI Dist TM (Vineland, NJ) distillation apparatus with the appropriate glassware for distillation. Temperature control, vacuum, and cold water.

Glassware including calibrated pipettes, volumetric flasks, etc.

6.0 REAGENTS

All reagents were of analytical grade or comparable purity.

Cyanide-free, reagent grade water prepared by a DI system, Type II or equivalent.

Sodium hydroxide, ACS Reagent Grade.

Sulfuric Acid – 18 N,

Dilute concentrated H_2SO_4, ACS Reagent Grade, 1 to1 with water.

Solutions for treating interferences.

Sulfide Test Paper is prepared as follows:

Lead acetate paper which has been previously moistened with acetic acid buffer solution is used.

If the paper darkens there is sulfide present in the sample. Add lead acetate solution or powered

lead carbonate and repeat the test until the paper does not darken.

Oxidizing Agent Test paper is prepared as follows:

Place a drop of the sampled water on a filter paper that had been pre-impregnated with KI solution followed by a starch solution. A blue color indicates the presence of oxidizing

agent(s). Keep the pre-impregnated paper in an amber vial under inert atmosphere.

Place a drop of the sampled water on a filter paper that had been pre-impregnated with KI solution followed by a starch solution. A blue color indicates the presence of oxidizing

agent(s). Keep the pre-impregnated paper in an amber vial under inert atmosphere.

Magnesium Chloride reagent solution:

Prepare by dissolving 510 gm of $MgCl_2 \cdot 6H_2O$ in reagent water and dilute to 1L. (Note: The reagent is required if it is known that iron cyanide complexes are present.)

Sulfamic acid:

Dissolve 20 gm reagent grade sulfamic acid in reagent water and dilute

to 1 Liter. Add when nitrates-Nitrites are present or suspected.

Stock cyanide solution – Dissolve approximately 1.6 g NaOH and 2.51 g KCN (ACS Reagent grade) in 1 Liter reagent water. Perform in the hood to avoid inhalation of KCN.

Standardize against silver nitrate standard as described below:

From the absorption solution take a measured volume of sample so that the titration will require approximately 1 to 10 mL of 0.02N $AgNO_3$ (that had been standardized against standard NaCl solution using K_2CrO_4 indicator) titrant. Dilute to 100mL using the NaOH dilution solution to be used for all titrations. For samples with cyanide concentration less than 5 mg/L do not dilute. As indicator, use HACH chloride 2 Indicator Powder Pillow.

Titrate with standard $AgNO_3$ titrant to the first change from canary yellow to a salmon (brown, orange) hue. Titrate also a blank containing the same amount of alkali and water as the standard.

Check titer weekly.

Standard cyanide solution.

Based on the concentration determined for the KCN stock solution calculate the volume required (approximately 10 mL) to prepare 1 Liter of a 10µg CN^-/mL solution. Use the following table to make standards.

Table1: Cyanide Standards -Kept in Fridge, recheck conc. of stock weekly.

Stock Solution (SS)	1 mL = 1 mg	1000 mg/L	2.51 g KCN in 1 L with 1.6 g NaOH	Weekly
Intermediate Solution (IS)	1mL = 10 ug	10 mg/L	5 mL of SS into 500 mL, use dilution solution	Daily
Working Solution (WS)	1 mL = 1 ug	1 mg/L	10 mL of IS into 100 mL, use dilution solution	Daily

Table 2. Calibration standards

Treat a series of labeled 50 mL volumetric flasks as follows.

mL of 1 mg/L into 50 mL	**mL of NaOH dilution solution**	**[CN^-] (mg/L)**
0 (blank)	40	0.00
1.0	39	0.02
3.0	37	0.06
5.0	35	0.10
7.0	33	0.14
10.0	30	0.20

Distillation **Reagents (kept in hood near MIDI-DIST)**

1.6 g/L NaOH

H_2SO_4, 18N (500 mL concentrated H_2SO_4 added dropwise to 500 mL H_2O on ice bath).

Acetate Buffer:

Dissolve 410 gm sodium acetate trihydrate in 500 mL reagent water

Color Reaction Reagents

Chloramine –T solution:

Dissolve 1.0 g of the anhydrous powder (or 1.25 g trihydrate) in 100 mL water.

Prepare weekly and store in the refrigerator.

Pyridine – Barbituric acid reagent:

Place 15 gm barbiteric acid in a 250 ml volumetric flask and add just enough water to wash sides of flask and wet the barbituric acid. Add 75 mL pyridine (ACS Reagent grade) and mix. Add 15 mL conc. HCL (Reagent grade), mix, cool to room temperature and dilute to volume. Add a magnetic bar and stir until the solution is clear.

Note: This solution is stable for up to 6 months if stored in amber bottle under refrigeration.

Discard if precipitate develops.

Sodium hydroxide solution: (Dilution Solution)

Dissolve 40 gm NaOH in 1 Liter reagent water. (1N)

Acetate Buffer Solution, pH 4.0 for sulfide screening.

Dissolve 146 grams of anhydrous Sodium Acetate ($NaC_2H_3O_2$) in 400 ml DI H_20, add 480 grams conc. Acetic acid and dilute to 1 L with DI H_2O.

Indicator Solution:

Dissolve 20 mg p-dimethylaminobenzalrhodanine in 100 ml acetone.

Calcium hydroxide, ACS Reagent Grade

7.0 PROCEDURE

Distillation:

Check pH of sample and record on raw data log. Then pipet 50 mL of sample into reaction flask.

Add 2-3 boiling chips and anti-foam if fatty acids are present.

Pipet 35 ml of dilution solution (1N NaOH) into Absorption flask.

Position the cold finger and absorption impingers.

Turn tap water on (50 to 60 gallon /hr flow rate).

Turn vacuum on, adjust each valve (1-2 bubbles per second at Absorption flask).

Add 0.2 grams of sulfamic acid through reagent inlet and wash down with D.I. H_2O.

Slowly add 5 mL 18 N H_2SO_4 through reagent inlet and wash down with D.I. H_2O.

Add 2 mL $MgCl_2$ solution through reagent inlet and wash down with D.I. H_2O. (If iron cyanide complexes are known to be present)

Let contents of boiling tube mix for three minutes before heating.

Set block temperature to 150^oC, turn heat on.

After 1 hr. turn heat off but keep the vacuum flowing for an additional 15 minute while cooling down.

The impinger solution should be disconnected slowly to prevent a back suck. Check the pH of the distillate and record on the raw data log. It is ready for analysis.

Continue to cool the block by water flow.

Transfer absorption quantitatively to 50 mL volumetric flask, using two rinses with dilution solution (total 5 mL) to affect the transfer.

Soak the impinger in reagent water immediately.

Analysis-EXPERIMENT

Proceed with 50 mL flasks containing calibration standards or samples.

Add 1 mL of acetate buffer (pH = 4.5).

Add 2 mL chloramine-T solution. Stopper, mix by inversion twice and let stand exactly 2 minutes.

Add 5 mL pyridine –barbituric acid reagent dilute to volume (50 mL) with reagent water, mix well and let stand for 8 minutes. Measure blank (0.0 mg CN^-/L.

Read absorbance of standards including the NaOH blank with a spectrophotometer zeroed using D. I. H_2O at 578nm and tabulate data on the appropriate form.

Read absorbance of samples with a spectrophotometer zeroed using D.I.H_2O at 578nm in the same manner and record the data on the form. Measure blank (0.0 mg CN^-/L).

7.3 Accuracy, Precision, MDL

Every 20th sample or every month:

Make a duplicate measurement (w/o distillation)

Spike a sample and measure recovery as follows:

Spike must be made *before* color reaction (and before distillation)

Aim to double [CN^-] in sample, otherwise middle of calibration.

Confer with spike table 5.

Table3: Spike Table mL of spike solution to add to 50 mL of sample in reaction flask before distillation.

$[CN^-]_{sam}$ mg/L	Spike soln 1000 mg/L	Spike soln 100 mg/L	Spike soln 10 mg/L
0.01	0.5 uL	5 uL	50 uL
0.05	2.5 uL	25 uL	250 uL
0.1	5 uL	50 uL	500 uL
0.2	10 uL	100 uL	1000 uL
0.5	25 uL	250 uL	2500 uL

Note: 100 mg/L may be prepared by a 1:10 dilution of stock solution. Note: Upper measurement limit is 0.2 mg/L. When needed, dilution may be performed in one of two ways: either of distillate with NaOH dilution solution, or of color-developed solution with color- developed blank. Be certain to record sample volume, spike solution volume, and spike solution concentration. Once per year, determine MDL.

8.0 Data Analysis and Calculations

Samples: Since absorption solution is brought to 50 mL in volumetric flask, concentration determined spectrophotometrically is equal to cyanide concentration in original solution if no dilution was made.

Duplicate:

$$\bar{x} = \frac{\left(\sum xi\right)}{N}$$

$$\%\ recovery = 100\,\frac{\left(C_{meas}V_{tot} - C_{sam}V_{sam}\right)}{\left(C_{spike}V_{spike}\right)}$$

where $V_{tot} = V_{spike} + V_{sam}$

Table 4. Calibration Curve

Standard Conc. (mg/L)	0.00	0.02	0.06	0.10	0.14	0.20
Absorbance@578 nm	0.0000	0.0912	0.2680	0.4102	0.5846	0.8398

R Squared (from instrument): R Squared (from Excel) : 0.9993

Scope: 4.1565

Intercept: 0.0054

Table 5. Sample Measurement

Test #	**Sample**	**Dilution Factor**	**Absorbance Reading**	**Cyanide (mg/L)**	**Final Conc Cyanide mg/L**
0	Blank	1.00	0.0000	0.0000	0.0000
1	sample	1.00	0.0427	0.0090	0.0090
2	Sample dup	1.00	0.0438	0.0092	0.0093
3 Check Std.	0.02 mg/L	1.00	0.0910	0.0206	0.0206
4 Check Std.	0.2 mg/L	1.00	0.8400	0.2008	0.2008
Sample for Spike					
5 Spike, MS		1.00	0.4430	0.1053	0.1053
6 Spike, dup. MSD		1.00	0.4452	0.1058	0.1059

Accuracy Check:

Average sample result: 0.0092 mg/L %RPD = 3.3%

Spike Concentration Calculations:

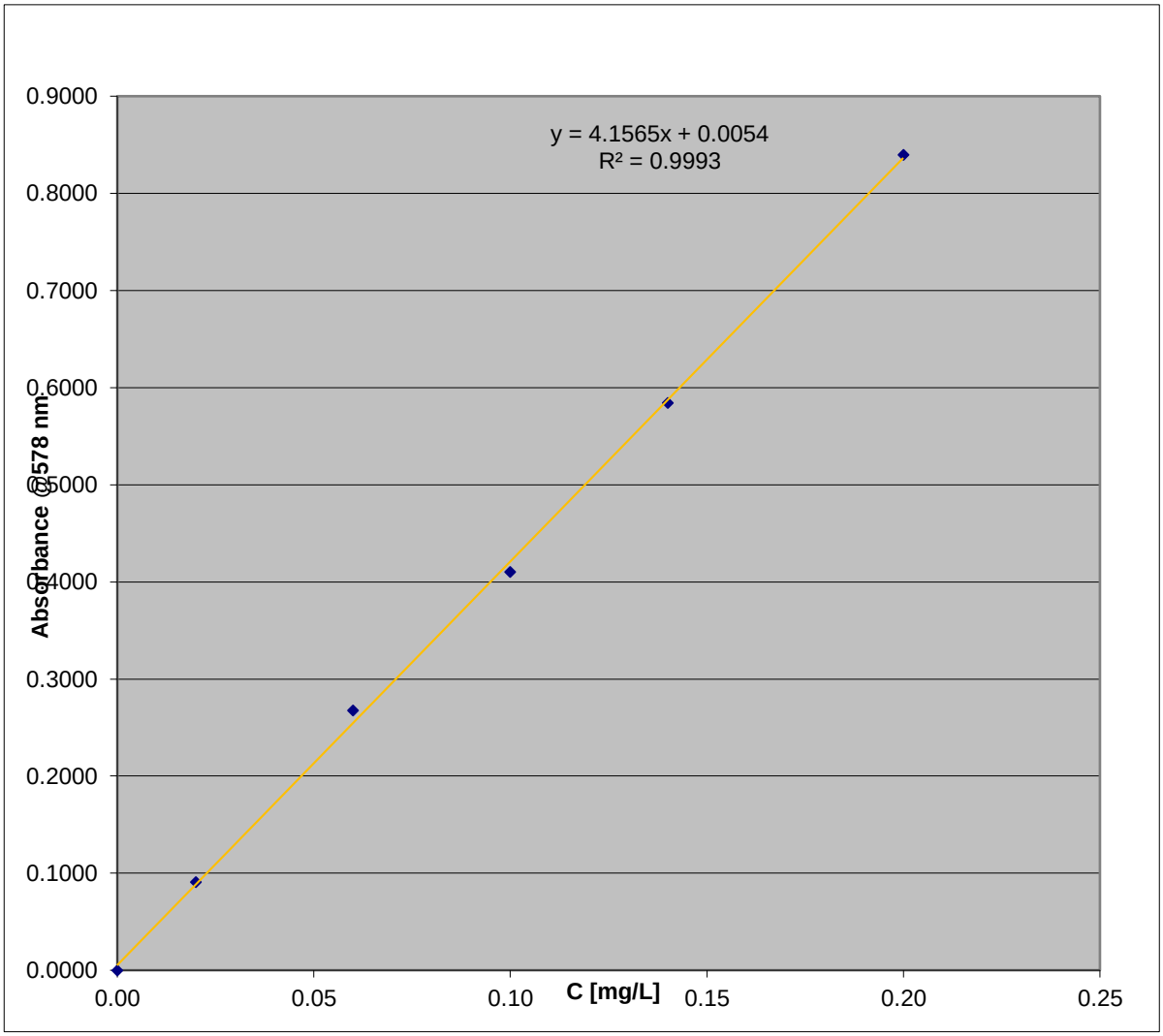
mL of Spiking Solution: 0.5 Sample Volume: 50 mL

Conc. Of Spiking Solution 9mg/L): 10.0

Matrix Spike Recovery (%): 96.30 % Average Spike Recovery %R=96.6%

Matrix Spike Recovery Duplicate: 96.9%

Firgue1: Calibration Curve



CALCULATIONS

Enter standards in excel spreadsheet to calculate correlation coefficient, slope and intercept. Correlation coefficient (r) must be greater than or equal to 0.995.

To calculate sample result:

mg CN^-/L= (A-b)/m*C

where:

A- Absorbance of sample

b- Intercept from linear regression

m- Slope from linear regression

C- Dilution factor (as applicable)

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 Run a method blank using 40 mL of NaOH dilution solution as the blank with each set of samples.

Determine precision and accuracy for every 20 samples or once a month if less than 20 samples are analyzed. Precision between the sample and duplicate must be less than 10% and the accuracy for the spike recoveries must be between 80-120%.

To determine accuracy run a method spike and spike duplicate. Perform the spiking every 20 samples or once a month if less than 20 samples are analyzed. Conduct the spike test after a sample result has been determined. Add enough spiking solution so that the added concentration (or absolute amount) is within the calibration curve.

A calibration curve must be analyzed every three months with a correlation coefficient of greater than or equal to 0.995.

A second source QC check must be analyzed every 20 samples or once a month if less than 20 samples are analyzed in that month. Recovery must be within 10% of the true value.

Each day samples are analyzed as a check standard from the same source as the curve must be analyzed. Recovery must be within 10% of the true value.

10. SAFETY AND WASTE DISPOSAL

It is desirable to conduct the analysis of unknown samples in a hood to avoid the possibility of generating HCN vapors (Toxic!!!) and minimize cross-contamination of samples.

Solutions containing samples and standards are oxidized in a hood to convert all cyanide to iso-cyanate and eventually to ammonium carbonate, using hydrogen peroxide or sodium hypochlorite. Pyridine (residual) is also destructed in the process before disposal.

11. RESULTS and DISCUSSION

Cyanide (CN^-) is the toxic chemical that may contaminate the drinking water, wastewater, or agricultural water. Cyanide is a fatal compound, and its acute poisoning is usually readily diagnosed. Cyanide enters air and soil from both natural processes and industrial activities. Most cyanide in surface water will form hydrogen cyanide (HCN) and evaporate [7]. An extractive spectrophotometric

method for the determination of cyanide in Passaic River wastewater is developed. This method is more sensitive as compared to other spectrophotometric methods for cyanide determination. The rapid color development, reproducibility, stability, and easy availability of the reagents are some advantages of the method. Industrial facilities who discharge wastewater to public waterways in the United States, stringent limits on cyanide, typically with monthly average effluent limits set around 0.005 ppm or less. If the total cyanide is **>0.2 mg CN-/L**, a measurement of free cyanide must be made using an approved free cyanide method to determine compliance [8]. The Cyanide result in Passaic River have been found 0.0090 mg/L, and 0.0093 mg/L, Percent average recovery 96.6%, and RPD% 3.33% (Table 5).

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