Nutrient Analysis in the Wastewater Laboratory

FVOA Mini-Conference 2012

Presenters: Mary Johnson & Connie Potter

Why Test for Ammonia & Phosphorus

Wastewater may contain high levels of ammonia and phosphorus. Releasing these nutrients to a receiving stream may lead to eutrophication.

eutrophication - a process by which pollution from such sources as sewage effluent or leachate from fertilized fields causes a lake, pond, or fen to become overrich in organic and mineral nutrients, so that algae and cyanobacteria grow rapidly and deplete the oxygen supply

Why Test for Ammonia & Phosphorus

Many new and renewal NPDES permits contain monitoring requirements for ammonia, phosphorus, and total nitrogen.

Ammonia Sources

- Municipal wastewater treatment plants
- Agricultural runoff (fertilizers & manure)
- Industrial discharges (paper mills, mines, food processing)

Phosphorus Sources

- Laundering or other cleaning
- Treatment of boiler waters
- Fertilizers (runoff)
- Water treatment chemicals

Ammonia Analysis

Standard Methods 4500 NH_3

- Titrimetric Method
- Ammonia Selective Electrode Method*
- Phenate Method

Ammonia Analysis
Sample Preservation and Storage

- If samples will be analyzed within 24 hours, refrigerate at 4 ^{o}C
- If samples will be analyzed after 24 of collection, acidify to pH < 2 with sulfuric acid and store at 4 ^{o}C.
- Preserved samples can be stored at 4 ^{o}C for up to 28 days.

Ammonia by ISE

Equipment

- pH/ISE Meter
- Ammonia ion selective electrode
- Stir plate
- Volumetric flasks
- Erlenmeyer flasks
- pipets

Chemicals

- Ammonia standard (1000 ppm)
- 10 N sodium hydroxide

Ammonia by ISE - Calibration

Prepare two standards.

The high standard should be 10 times the concentration of the low standard.

Use volumetric glassware.

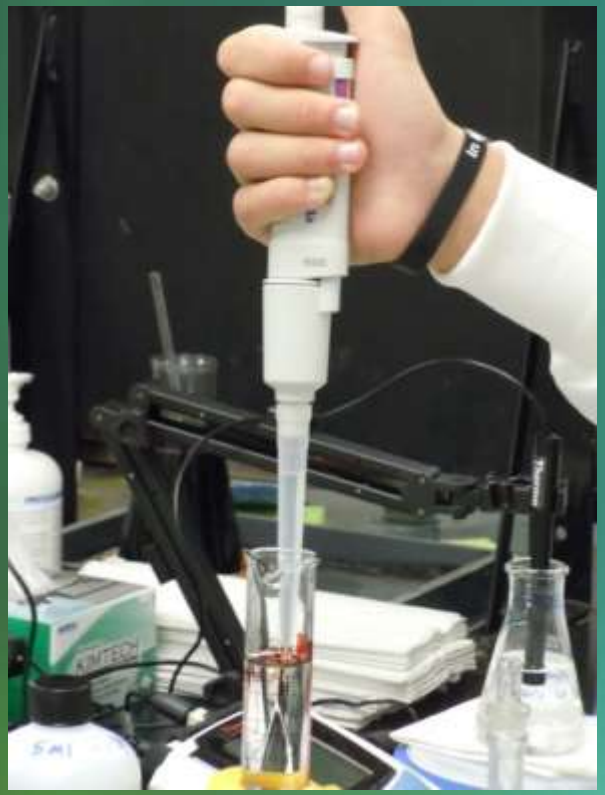
RRWRD uses 2.0 mg/L & 20.0 mg/L standards.

Ammonia by ISE - Calibration

Follow directions supplied with your specific ion meter to calibrate meter.

General Directions

- Pour 100 mL of each standard in an erlenmeyer flask.
- Place low standard flask on stir plate and stir moderately
- Insert electrode in sample
- Add 10 N NaOH.
- Allow meter to stabilize.
- Enter reading.
- Repeat for high standard



pipetting standard

diluting standard

transferring standard to flask

adding sodium hydroxide

waiting for meter to stabilize

Ammonia by ISE - Calibration

Slope is the change in millivolts observed with every tenfold change in concentration.

An acceptable slope is -54 to -60 at 25 ± 5°C.

Do not analyze samples unless your slope is acceptable.

Ammonia by ISE - Samples

General Directions

- Pour 100 mL of sample into an Erlenmeyer flask.
- Place flask on stir plate and stir moderately
- Insert electrode in sample
- Add 10 N NaOH.
- Allow meter to stabilize.
- After meter has stabilized, record ammonia concentration.

Ammonia by ISE – Sample Pretreatment

You can eliminate interferences with preliminary distillation.

<u>General Directions</u>

- Pour sample into Kjeldahl flask. Dilute if necessary
- Add borate buffer to sample
- Adjust pH to > 9.5 with 6 N NaOH
- Attached flask to distillation apparatus.
- Distill.
- Collect distillate in 0.1% sulfuric acid.

Ammonia by ISE – Sample Pretreatment

Ammonia by ISE – solid samples

You can determine the ammonia present in sludge using pre-distillation.

Just weigh the sample before adding it to the Kjeldahl flask.

Ammonia by ISE - Calculations

Undistilled samples:

Meter reading * 100 mL/sample volume

Distilled samples: assume sample volume = 500 mL
distillate volume = 100 mL

Liquids

Mtr reading * 500 mL * 100 mL/(mL spl * mL distillate)

Solids

Mtr reading * (500 mL * 100 mL)/(g spl * %TS * 0.01 * ml distillate)

Ammonia by ISE – Analysis Range

Low Level

- Use an approved EPA procedure to determine your method detection limit (MDL)

  (RRWRD MDL is 0.1)
- Your reporting limit is typically about 3 times your MDL.

High level

- High end of range is your high standard.

  (RRWRD high is 20 mg/L.)
- You can extend high end of range by using a smaller sample volume and diluting it to 100 mL.

Ammonia by ISE – Helpful Hints

- All samples and standards should be at the same temperature (preferably room temperature.)
- Use the same volume for standards and samples (usually 100 mL.)
- Use pH indicating ionic strength adjuster rather than 10 N NaOH
- Make sure readout is stable before recording ammonia concentrations. Samples with low ammonia levels may take more than five minutes to stabilize.
- Dirty samples can foul the electrode membrane.

Phosphorus Analysis

Know what you want to analyze.

- Total reactive phosphorus
- Total acid –hydrolyzable phosphorus
- Total phosphorus
- Dissolved reactive phosphorus
- Dissolved acid-hydrolyzable phosphorus
- Dissolved phosphorus
- Suspended reactive phosphorus
- Suspended acid-hydrolyzable phosphorus
- Suspended phosphorus

Phosphorus Analysis

Standard Methods 4500-P

- Vanadomolybdophosphoric Acid Method (1 – 20 mg/L)
- Stannous Chloride Method (.01 – 6 mg/L)
- Ascorbic Acid Method (.01 – 6 mg/L)*

Hach 8190 – equivalent to *Standard Methods* 4500-P ascorbic acid method

Phosphorus Analysis

If you want to analyze for any form of phosphorus other than total reative phosphorus, you must pre-treat the sample.

Pretreatment may include

- Filtration
- Acid hydrolysis
- Digestion

Total Phosphorus Analysis
Sample Preservation and Storage

- Preservation – Adjust pH < 2 with hydrochloric acid

- Storage - Store at 4 ^{o}C for up to 28 days

- Note: Samples can leach phosphorus from plastic containers. Use glass containers for samples with low phosphorus levels.

Total Phosphorus using Hach

(ascorbic acid colorimetry)

Supplies

- Heating block (Hach COD reactor)
- Spectrophotometer
- Auto-pipetters

Reagents

Hach Total Phosphorus Test N Tube Reagent Set includes reaction vials, potassium persulfate packets, sodium hydroxide, and ascorbic acid packets.

Total Phosphorus – Hach Procedure

General Directions

- Add 5 mL sample to digestion vial
- Add potassium persulfate powder. Shake to mix.
- Heat vial for 30 minutes
- Add 2 mL NaOH
- Add PhosVer 3 reagent
- Allow color to develop for 2 minutes
- Read concentration using spectrophotometer. Wavelength is 650.

adjusting auto-pipetter

pipetting samples

adding reagents

hot block digestor

adding sodium hydroxide

shades of blue

spectrophotometer

Total Phosphorus - Hach Procedure Calculations

Hach spectrophotometers will provide a readout in mg/L P.

Dilutions:

$$\text{mg/L P} * \frac{5\ \text{mL}}{\text{sample volume}}$$

Total Phosporus - Hach Procedure Analysis Range

Phosphorus: 0 – 1.10 mg/L P

Phosphate: 0 – 3.50 mg/L PO_4^{3-}

You can extend the range by diluting samples before analysis.

Total Phosphorus – Hach Procedure Helpful Hints

- Let heating block warm up for at least 10 minutes before inserting sample vials
- Shake samples well before pipetting sample aliquot.
- You can complete the procedure through the digestion step, and then finish it the next day.
- If there is sediment present in sample, make sure it is settled to bottom of tube before reading on the spectrophotometer.
- Read sample between 2 and 8 minutes of adding PhosVer3 powder pillow. This means you may have to be reading one sample while still adding reagent top others.

Total Phosphorus for Solids

(ascorbic acid colorimetry)

Supplies

- Heating blocks
- UV/VIS Spectrophotometer
- Auto-pipetters
- Kjeldahl flasks
- Nessler's tubes

Reagents

- Phenolphthalein Indicator
- Concentrated H_2SO_4
- 10 N NaOH, Concentrated HNO_3
- 5N H_2SO_4
- Potassium Antimonyl Tartrate
- Ammonium Molybdate,
- Ascorbic Acid.

Total Phosphorus – Solids

Digestion

- Add sample to Kjeldahl flask and bring volume up to 200 mL with DI water. Add 2 mL of concentrated H_2SO_4 and 5 mL concentrated HNO_3. Swirl to mix.
- Digest on a heating unit. Digestion is complete when solution is colorless and fumes are white. Cool.
- Add 20 mL DI water and few drops of phenolphthalein indicator. Add enough 10 N NaOH to produce a pink color.
- Quantitatively transfer solution to a 100 mL Volumetric flask.

Total Phosphorus – Solids

Colorimetry

- Pipet appropriate volume of digested samples into Nessler tubes. Add 5 N drop wise to discharge pink color. Adjust volume 50 mL with DI water.
- Add 8 mL of the color reagent and mix.
- Allow color to develop for 10 minutes but no longer than 30 minutes.
- Read concentration using spectrophotometer. Wavelength is 650.

$$\text{mg/Kg P} = \frac{\text{ug P}}{\text{mL colorimetry}} \times \frac{100\ \text{mL}}{\text{g spl} * TS * 0.1} \times \frac{1\text{mg}}{1000\text{ug}} \times \frac{1000\text{g}}{1\text{Kg}}$$

1.

2.

3.

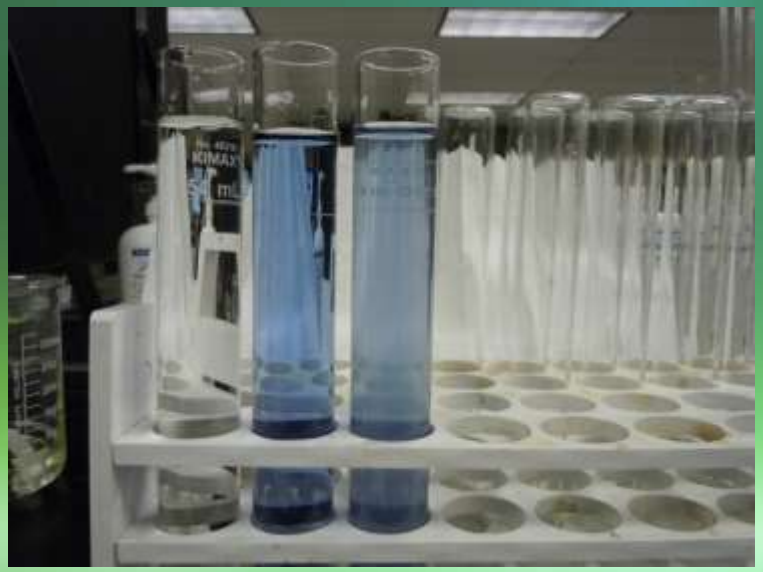
1. weighing solid sample
2. adding water to sample
3. adding acid to sample

digesting samples

digestion almost complete

completely digested sample

pH adjusted digestate



1. Transferring sample from Kjeldahl to flask
2. Nessler tubes with pH adjusted samples
3. Samples after adding colorimetry reagents

Quality Control

It is good practice to include the following in each analysis batch:

- Laboratory Control Sample (LCS) – this is a purchased solution of know concentration. Run it immediately after calibrating the meter.

- Blank – ammonia free water

- Matrix Spike Duplicate (MSD) – these are samples spiked with a know concentration of ammonia

- Continuing Calibration Verification (CCV) – this is usually a standard made in house. Run it after you read all the samples.

Quality Control

How do you know if your analysis batch is “good?”

- LCS meets the manufacturer’s acceptance limits.
- Blank is less than half of the method detection limit.
- MSD recovery is 80 – 120%.
- CCV recovery is 90 – 110 %.

Total Nitrogen

Many new and renewal permits include a Total Nitrogen monitoring requirement.

Total Nitrogen is organic nitrogen + ammonia + nitrate + nitrite

Total Nitrogen Analysis

Typically labs determine total nitrogen by analyzing for Kjeldahl nitrogen (digestion followed by distillation) and nitrate/nitrite (using the cadmium reduction method.) These are traditional, wet lab analyses

Some labs use ion chromatography to analyze for total nitrogen.

The RRWRD send its total nitrogen analyses to a contract lab.

Contact Information

Mary Johnson:

mjohnson@rrwrd.dst.il.us

Connie Potter:

cpotter@rrwrd.dst.il.us

Rock River Water Reclamation District