Nitrogen

VT WSMD Wastewater Program Lab Manual Section #14

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Nitrogen

Nitrogen limits are included in most Vermont NPDES permits, particularly those in the Long Island Sound Watershed. Whereas Phosphorus is often the "limiting factor" considered responsible for eutrophication and algal blooms in fresh waterbodies such as Lake Champlain, nitrogen is considered the limiting factor responsible for these problems in salt water. Both nutrients play a role in creating eutrophication and algal blooms.

Under "normal conditions" in nature Phosphorus and Nitrogen are not available in concentrations sufficient to allow widespread algal blooms. Nutrient concentrations rise significantly due to runoff from impervious surfaces, dirt roads, farms, fertilized lawns, and other sources that enter the water body.

In wastewater we are primarily concerned with four forms of nitrogen: ammonia, organic nitrogen, nitrites, and nitrates. The Total Kjeldahl Nitrogen (TKN) analysis measures ammonia and organic nitrogen. The nitrite and nitrate (NO_x) analysis convert all nitrites to nitrates and the result includes the sum of both forms. In order to "speciate" or measure each of the two forms the nitrite and nitrate analyses must be performed individually.

NOTE: Total Nitrogen is the sum of Total Kjeldahl Nitrogen, Nitrites and Nitrates. **If ammonia is analyzed separately be sure NOT to include the ammonia result in the Total Nitrogen result as it is already included in the TKN**!!

Remember; $TN = TKN + NO_2 + NO_3$

TKN = Ammonia + organic nitrogen

Ammonia Nitrogen

Ammonia, (NH3) is a very important parameter to be analyzed at wastewater facilities. It is extremely toxic to aquatic organisms, and analysis can be very informative regarding the effectiveness of treatment. Finding excessive ammonia in facility effluent suggests the facility is failing in the breakdown of ammonia to nitrites and nitrates. The efficiency of nitrification can further be established by measuring concentrations of nitrite (NO2) and nitrate (NO3). High nitrites in effluent can indicate a lack of complete nitrification which is a serious problem. This will be discussed further in the appropriate section of this manual.

The concentration and presence of interferences in the sample determine the method used for analysis. Whereas the selective ammonia ion electrode method is acceptable and has been used by some Vermont wastewater facilities, many operators have found it to require excessive maintenance and affected by many interferences. Likewise, the titrimetric method has been determined by most operators to be too time consuming, cumbersome and requires distillation of the sample before analysis. **Note:** For all of these methods it is important to use ammonia free distilled water. **Deionized water is not recommended as it often contains ammonia. Also samples from each individual facility must be proven to NOT contain interferences in such quantity as to adversely affect analytical results.** That can be accomplished by performing the analysis on distilled vs. non- distilled samples. If results do not vary significantly (<10% is ok) analyses may be performed without distillation.

For instructions regarding distillation: refer to Standard Methods for Examination of Water and Wastewater 23rd edition section 4500 NH3 B

Interferences: There are many substances that can interfere with the ammonia analysis. These include urea, glycine, glutamic acid, cyanates, acetamide, chlorine and others depending upon the method used. It is very important to dechlorinate the sample immediately upon collection if a residual chlorine is expected.

Hold Time: Best results are obtained from samples that are analyzed immediately. If this isn't possible the unacidified sample should be refrigerated at 6 °C and analyzed within 24 hours.

Procedures: At this time Vermont facility operators seem to prefer the Hach® Test 'n Tube methods for ammonia analysis. A link to that method is provided here. Keep in mind that this method uses deionized water as a blank with a blank correction. **It is preferred to use ammonia free distilled water for all ammonia analyses. ALSO keep in mind that this method is an "equivalent method". That means that it is generally accepted IF quality control practices are equivalent to the original method. Check with your assigned Wastewater Program analyst to assure the method is accepted for NPDES reporting purposes.**

Since the Hach TNT methods for many parameters have become so widely used by Vermont wastewater operators it seems prudent to attempt to clear up some of the confusion regarding acceptability of these methods. Several Hach methods are EPA approved and acceptable for compliance reporting according to 10 CFR part 136. However, many are not. Whereas Hach methods are generally very good, simplified methods designed to be easy to use while generating valuable results, the nomenclature used in describing the acceptability is somewhat confusing.

For example: The Hach TNT Plus (tm) 830/831/832 Ammonia Method 10205

The three different numbers refer simply to different concentration ranges.

"Method" 830 range = 0.015-2.00mg/L NH3-N

"Method" 831 range = 1 – 12 mg/L NH3-N

"Method" 832 range = 2 – 47 mg/L NH3-N

Method 10205 is considered by Hach to be equivalent to EPA methods 350.1, 351.1, and 351.2 for the purposes of regulatory reporting of Ammonia (as nitrogen) and Total Kjeldahl Nitrogen to the original EPA method.

In a 2007 EPA memo the EPA stated that the chemistry is equivalent to those methods. Hach method 10205 does not appear in 40 CFR 136. BUT in using this method it is acceptable to cite EPA method 350.1, 351.1, or 351.2 **ONLY IF** the quality control procedures from the original EPA methods are used.

Bottom line: This Hach method and associated procedures are acceptable as long as quality control requirements from the original EPA methods are met.

The link to the Hach® TNT method 830 for low range ammonia is:

https://www.hach.com/asset-get.download-en.jsa?id=19556239154

For higher ranges download Hach methods 831 or 832

Here's a link to Hach® method 832 for high range ammonia:

DOC312.53.94127_1Ed_TNT832 (3).pdf

Nitrites/Nitrates

The analysis for nitrite **and** nitrate (NO_x) converts all nitrites to nitrates and the result includes the sum of both forms. In order to "speciate" or measure each of the two forms the nitrite and nitrate analyses must be performed individually. At this point in time most NPDES permits do not require "speciation". Therefore, the combined Nitrite/Nitrate analysis is often the method chosen by operators.

Actually "speciation", the measurement of nitrites and nitrates separately, can be quite useful to operators as measurement of nitrites can help identify problems with the process (such as incomplete or lack of nitrification). In at least one case at a Vermont wastewater facility this knowledge could have saved the municipality a great deal of time, money, and frustration. In that case, more and more chlorine was needed to produce the required chlorine residual to provide an acceptable coliform "kill". The facility dug up the chlorine line, suspecting a leak underground. As it turned out there was no leak. In fact, the problem was a loss of nitrification at the facility. Incomplete nitrification occurs when the oxygen concentration is insufficient to convert nitrites to nitrates. The problem is compounded because nitrites act as a "chlorine sponge." In fact, it requires at least 6 times as much chlorine to produce a residual in "partial nitrification" situations.

Partial nitrification can be caused by a number of factors including cold temperature, nutrient deficiencies, high influent ammonium, toxicity, pH changes, insufficient retention time in the aeration tank, very high soluble BOD or low Dissolved oxygen. Also, nitrites can be toxic to aquatic organisms **AND** wastewater organisms including floc-forming bacteria* (from Climate Policy Watcher article, link below). Obviously, analysis of nitrites can be a very useful process control tool.

*For more information regarding nitrification there is an excellent article in "Climate Policy Watcher" entitled Nitrite Ion Accumulation. The link is:

- Nitrite Ion Accumulation - Nitrification - Climate Policy Watcher (climate-policy-watcher.org)

The most commonly used method at Vermont wastewater facilities for Nitrite/Nitrate analysis is the Hach TNT 835/836 method 10206. This method converts the nitrite to nitrate to give a combined nitrite/nitrate result. Nitrite levels in exceedance of 2 mg/L interfere with the analysis. A procedure for elimination this interference is provided in the method description. But how would you know there was a nitrite interference without performing the separate nitrite analysis? The good news is that under "normal conditions" nitrite levels would be far less than 2 mg/L. Keep in mind that this analysis is

delegated as “equivalent” by the Hach company. Therefore, be sure to check with the assigned Wastewater Program analyst for acceptability regarding NPDES reporting purposes.

Here is a link to Hach TNT 835/836 method 10206 for determination of nitrite/nitrate:

Hach Nitrate Method 10206 Final 01102013 (1).pdf

Nitrite (NO_2^-)

As mentioned earlier, the nitrite analysis can be very useful. There is a colorimetric method described in section 4500 NO2 B in Standard Methods For Analysis of Water and Wastewater The method requires the use of nitrite free distilled water which is very difficult to prepare in most wastewater facility situations. For that and other reasons most Vermont wastewater technician prefer to use the Hach TNT 839 method. The Hach methods make use of “reagent blanks” to negate color, turbidity and other interferences that might be found in the reagents themselves. The result of the reagent blank is then subtracted from the sample result. This allows for the use of deionized water as a “reagent”.

This method is described as “equivalent” to EPA method 10207. Be sure to check with the assigned Wastewater Program analyst for acceptability regarding NPDES reporting purposes. Quality control requirements are described in the method. Be aware that Hach® recommends that standards for this analysis be prepared from directions in section 4500-NO2 B of Standard Methods for the Examination of Water and Wastewater

https://www.hach.com/asset-get.download-en.jsa?id=7639982523

Preservation

Note: Never use acid to preserve a sample for nitrite analysis. This could cause conversion of nitrites to nitrates.

Analyze samples for nitrite as soon as possible to prevent bacterial conversion of nitrites to nitrates.

Nitrate (NO_3^-)

Most of the methods described in 4500-NO3 of Standard Methods For the Analysis of Water and Wastewater are for one reason or another not very practical for in-house analysis at wastewater facilities. The Ultraviolet Spectrophotometric method is for samples with very low organic material (i.e. drinking water or uncontaminated natural water). The Nitrate Electrode method requires that temperature variations between sample and standards be kept within +/- 1°C, sample pH must be held constant, and the ionic strength of the sample and standards must be constant.

The most commonly used method for nitrate analysis performed at Vermont wastewater facilities is Hach TNT method 10206. The acceptability information noted below is taken from the Hach® website.

Method 10206 using the Nitrate TNTplus Vial Test, LR (0.2-13.5 mg/L NO3-N) and Nitrate TNT plus Vial Test, HR (5-35 mg/L NO3--N); (Product # TNT835 and TNT836) is **EPA approved** for drinking water cited

in the 40 Code of Federal Regulations (CFR) 141 and is approved for wastewater cited under 40 CFR 136 (Clean water Act).

A link to this method is provided here:

https://www.hach.com/asset-get.download-en.jsa?id=7639983742

Preservation:

- It is important that the sample be analyzed within 3 hours for this analysis (method).
- It is very important that the sample be between 20℃ and 23℃ before the analysis is performed for this method.
- Nitrite concentrations >2 mg/L will interfere with this method.

*These preservation requirements apply specifically to the Hach TNT plus method .

Total Nitrogen

Total nitrogen is the sum of Total Kjeldahl Nitrogen, NO2 and NO3. It can be calculated from the results of those analyses performed by any of the methods described in 40 CFR 136 **OR** A Total Nitrogen analysis can be performed using a method such as Hach TNT for Total Nitrogen Persulfate Digestion Low range method 10071. The low range method has a range of 0.5 to 25mg/L N.

Be aware that at this time Hach method 10071 is not approved by EPA. It has not received "Hach's®" rating of equivalent and therefore its acceptability for NPDES reporting is not approved by the VT DEC. This could change. Be sure to check with the VT DEC before reporting results of this analysis for NPDES report purposes.

The link to the Hach TNT Persulfate Digestion method 10071is:

https://www.hach.com/asset-get.download-en.jsa?id=7639983804https://www.hach.com/asset-

A method description offered by the Hach® Company describes this method as using" an alkaline persulfate digestion under heat to convert all forms of nitrogen to nitrate. Chromotrophic acid is then added to react with nitrate and form a yellow complex with an absorption of 420nm."

Method 4500 N-C in Standard Methods For Examination of Water and Wastewater does describe a persulfate digestion method in which "total nitrogen is determined oxidation of all nitrogenous compounds to nitrate by alkaline oxidation at 100 to 110℃.

Kjeldahl Nitrogen: Semi-Micro Kjeldahl Method and Ion Selective Electrode Method

Background

Nitrogen is often the limiting factor in biological systems, especially systems that depend on bacteria for the breakdown of substances. Knowing how much nitrogen is present in a system can be very useful because a deficient supply of nitrogen can result in the inability of bacteria to grow.

Total Kjeldahl Nitrogen includes organic nitrogen compounds as well as ammonia nitrogen. This procedure allows for the measurement of nitrogen in amino acids, proteins, peptides and ammonia.

Many Vermont wastewater facilities performing in house nitrogen analysis at this time are using the Hach® TNT method for nitrogen analysis. For Total Kjeldahl Nitrogen, Hach® TNT 880 Method 10242 is often used. Here is a link to that method:

http://www.hach.com/simplified-tkn-s-tkn-tntplus-vial-test-0-16-mg-l-n-25-tests/produc…

After clicking on that link download the "Methods and Procedures" to see instructions for the analysis.

The ion selective electrode method described here is another method used at Vermont wastewater facilities for the determination of Total Kjeldahl Nitrogen. Digestion and distillation are required in all TKN methods for NPDES testing. After digestion and distillation, the following methods of TKN determination are also acceptable Titration, automated phenate, semi-automated block digester or potentiometric

Interferences

1. Metals: The interference from metals can be eliminated with the addition of the NaI EDTA solution.
2. *High Nitrate Concentrations: Nitrate more than 10 mg/L can cause a negative interference. This interference can be eliminated by running the sample through an anion exchange resin (chloride form) to remove the nitrate prior to TKN analysis.
    a. Unfortunately, this technique is far less successful when analyzing wastewater samples when the suspended solids concentration is high.
3. Organic Matter: Large amounts of organic matter can cause a positive interference. To negate this interference, add 10 mL concentrated H_2SO_4 to the digestion flask per gram of organic matter. (The organic matter can be estimated from COD results by assuming that 3 grams COD equals 1 gram of organic matter.)
4. Inorganic salts and solids cause boiling temperature to rise causing pyrolytic loss of nitrogen - addition of more H_2SO_4 gives reasonable results (1 mL additional H_2SO_4 per gram of salt).

    *NOTE: If acid addition is necessary for sample analysis the same volume of acid should be added to the blank.

Equipment

- pH Meter - capable of accepting ion selective electrodes and measuring in millivolt units.
- Ammonia probe - such as the Orion 95-10

- Magnetic Stirring Device - with TFE coated stirring bar
- Digestion apparatus - A Kjeldahl digestion apparatus with appropriately sized digestion flasks and suction to remove SO_3 fumes and water.
- Block digester (Technicon BD-40) or individual heating elements or hot plates
- Various graduated and volumetric pipets

Reagents

*NOTE: If samples are to be distilled see additional reagents list in Appendix A (as required for NPDES testing).

- Ammonia Free Distilled Water
  - Traces of ammonia in distilled water can be removed by adding 0.1 milliliter concentrated H_2SO_4 per liter to distilled water and redistilling. It's a good idea to throw out the first 100 milliliters of the distillate.
- Mercuric Sulfate Solution
  - Dissolve 8 grams mercuric oxide (HgO) into 100 milliliters *6N H_2SO_4. This solution can be kept refrigerated at 4□C for up to one year.
  - *6N H_2SO_4 is prepared by pouring 167 milliliters concentrated (36N) H_2SO_4 into a one-liter volumetric flask containing about 500 milliliters distilled water. Then bring the total volume to one liter with distilled water.
- Digestion Reagent
  - To 650 milliliters distilled water add 200 milliliters concentrated H_2SO_4 **CAREFULLY!**
  - Dissolve 134 grams K_2SO_4 into the dilute H_2SO_4 solution
  - Then slowly add, while stirring, 25 milliliters of the mercuric sulfate solution (from #2 above). Dilute this solution to one liter with distilled water. This solution should be stored at room temperature to prevent crystallization. It can be kept for three months.
- 10N NaOH
  - Two liters of 10 N NaOH can be prepared by partially filling a two-liter wide mouth flask with distilled water. Adding 800 grams NaOH and diluting to two liters with distilled water. This solution can be stored at room temperature for up to six months.
- 10N NAOH, NaI, EDTA Solution
  - NOTE: This solution is needed only if interference from metals is suspected in the sample.
  - To approximately 500 milliliters distilled water add 800 grams NaOH, 600 grams NaI, and 4 grams EDTA. Dilute to 2 liters with distilled water. This solution can be stored for up to six months at room temperature.
- Stock $(NH_4)_2\ SO_4$ Standard Solution 100 mg/liter TKN-N
  - Dry $(NH_4)_2SO_4$ for at least one hour at 105□C. Cool for one hour in a desiccator.
  - Weigh out 0.4706 grams $(NH_4)_2SO_4$ add this to approximately 500 milliliters distilled water and dilute to one liter with distilled water. This solution can be stored for 30 days refrigerated at 4□C.
- Working $(NH_4)SO_4$ Standard Solution 10 mg/liter TKN-N
  - Dilute 10 milliliters of the stock $(NH_4)_2\ SO_4$ standard solution to 100 milliliters with distilled water. This solution must be used the day it is prepared.

- Calibration Standards
    - (select 5 from table which bracket analytical range.)

	Value of Std. in mg/l	mg/50 mL	100 mg/l Std. per 50 mL	10 mg/l Std. per 50 mL
	30 mg/l	1.5 mg	15 mL	
	20 mg/l	1.0 mg	10 mL	
**********	10 mg/l	0.5 mg	5 mL	
	8 mg/l	0.4 mg	4 mL	
	7 mg/l	0.35 mg	3.5 mL	
Normal range of wastewater	4 mg/l	0.2 mg	2 mL	
	2 mg/l	0.1 mg		10 mL
	1 mg/l	0.05 mg		5 mL
	0.6 mg/l	0.03 mg		3 mL
**********	0.5 mg/l	0.025 mg		2.5 mL
	0.4 mg/l	0.02 mg		2 mL
	0.2 mg/l	0.01 mg		1 mL

Procedure

1) Digestion
    a. On the day the analysis will be performed, rinse boiling flasks with dilute acid (10% H_2SO_4 or 20% HCL). Rinse three times with distilled water.
    b. Using the table provided, prepare 5 calibration standards suitable to the expected range of samples to be analyzed.
    c. Shake samples vigorously before dispensing via a graduated cylinder. 50 mL is total volume. If dilution is needed, use less and record the dilution factor on the data sheet.
    d. To each flask, add boiling stones and 10 mL of digestion reagent. (Wide-mouth serological pipettes give the quickest delivery.)

e. Turn on vacuum for all digestion racks that are to be used - plug the unused manifold intakes with empty digestion flasks. Adjust the boiling rate and allow to boil until the solution clears or is pale straw color.
f. Heat the solution for 30 minutes after the dense white SO_3 fumes appear.
g. Allow flasks to cool.
h. If you are using the type of flask that the ammonia probe can fit into, simply dilute to 50 milliliters with distilled water (in the flask); cover and refrigerate.

If the probe will not fit into the flask: Measure out 44 milliliters distilled water into a graduated cylinder. Use this volume of distilled water to wash the contents of the digestion flask into a clean dry container capable of accommodating the ammonia probe. Refrigerate. This is a good stopping point if the procedure cannot be finished in one day. If distillation is required, go to Appendix A; if not, proceed to Section 2.

2) TKN Ammonia Probe: <u>METER CALIBRATION</u> (probe should be stored in filling solution when not in use).
a. Let the meter warm up for about 20 minutes before reading. Change the filling solution before each probe use (2.5 mL).
b. Place 100 mL distilled water into a 200 mL Berzelius beaker. Add a magnetic stirring bar.
c. Using a graduated pipette add 1 mL 10 N NaOH while stirring.
d. Place washed/dried probe into solution. Then set the meter to REL MV scale. Check for air bubbles on the probe membrane. If there are bubbles present remove them by gently tapping the probe against the side of the beaker or by removing and then reinserting the probe. Most ammonia probes are designed with a method for removing air bubbles from the probe body. Usually, this can be accomplished by gently pulling up on the probe lead wire and releasing.
e. Using a volumetric pipette add 1.0 mL of 100 mg/L $(NH_4)_2SO_4$ stock solution into the beaker.
f. Wait for the meter to stabilize then adjust the meter to read 000.0 by turning the calibration knob or pushing the zero button.
g. Using a 10.0 mL volumetric pipette transfer 10 mL of 100 mg/L $(NH_4)_2SO_4$ stock solution into the beaker. Once the meter stabilizes record the volume on a data sheet. The calibration is okay if the reading is -57.0 mv +/- 3 mv. If the response is slow the membrane should be changed according to instructions in the Ammonia Probe instruction pamphlet. If -57.0 ± 3 mv cannot be achieved, do an inner body check as outlined in the pamphlet. If that fails several times, a new probe will have to be purchased.

3) TKN Ammonia Probe: Sample Analysis (Treat standards exactly the same as samples.)

<u>IMPORTANT NOTE:</u> If samples are distilled use only 1 mL of NaOH. If samples are not distilled use a total of 10 mL NaOH as described below.

a. Add 6 mL 10 N NaOH to each Nalgene bottle containing digested sample.
b. Cool digested samples and standards in ice bath. Standards and samples should be at the same temperature.

c. Place a stir bar into the sample, place the rinsed and dried probe below the sample surface. Check for bubbles on the probe membrane - remove any bubbles by tapping the probe against the bottle (keeping the stir bar at the lowest possible RPM while providing adequate mixing will help cut down on bubble formation).

d. Allow the meter to recover to a value at least as positive as the value corresponding to the lowest concentration standard.

e. **If sample is suspected of containing interfering metals**:
Inject 4 mL 10 N NaOH, NaI, EDTA into sample using a graduated pipette. Check for air bubbles.

If sample does not contain interfering metals:
Inject 4 mL 10 N NaOH solution into sample using a graduated pipette. Check for air bubbles.

If you are unsure whether or not the sample contains metals:
Use the NaOH, NaI, EDTA solution.

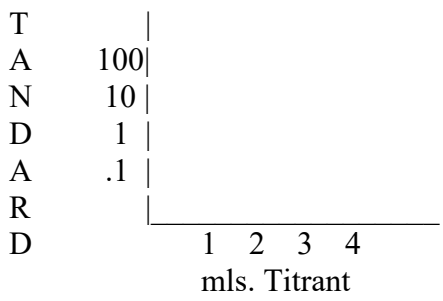
f. Record the lowest (most negative) MV reading. Be sure to watch the meter carefully so as not to miss the "bottom".

g. After removing the probe and stir bar from the sample, rinse and dry.

Calculations

Plot a curve for your standards, using semilogarithmic graph paper or using Excel with a log scale on the Y axis.

Example:



Then from this curve obtain your sample results.

Then calculate your final result by applying this formula.

$$NH_3 - N\frac{mg}{L} = A * B * \left(\frac{101 + C}{101}\right)$$

Where:

A = dilution factor

B = concentration of NH_3-N mg/L from calibration curve

C = volume of 10 N NaOH added in excess of:

- 1 mL if the sample was distilled **OR**
- 10 mL if the sample was not distilled

Total Kjeldahl Nitrogen (Ion Selective Electrode Method) Troubleshooting Guide

NOTE: This troubleshooting guide has been taken in its entirety from the Orion Model 95-12 Ammonia Electrode Instruction Manual.

PROBLEM	MOST LIKELY CAUSE	SOLUTION
Off-scale or over-range reading	Defective Meter	Perform meter checkout procedure (see meter instruction manual)
	Defective inner body	Refer to Troubleshooting Guide (check inner body operation)
	Electrodes not plugged in properly	Unplug electrodes and reseat
	Internal filling solution not added	Fill outer body of electrode with proper amount of internal filling solution
	Air bubble on membrane	Remove bubble by redipping electrode
	Electrodes not in solution	Put electrodes in solution
Noisy or unstable readings (erratic - rapidly changing)	Insufficient internal filling solution	Fill outer body of electrode with proper amount of interal filling solution
	Defective Meter	Perform meter check out procedure (see meter instruction manual)
	Bottom cap loose	Ensure that bottom cap is screwed on tight enough to close gap between bottom cap and body
	Defective inner body	Check inner body operation
	ISA not used	Use recommended ISA, Orion Cat. No. 951211
	Meter or stirrer improperly grounded	Check meter and stirrer for grounding

PROBLEM	MOST LIKELY CAUSE	SOLUTION
Drift (Reading slowly changing in one direction)	Internal filling solution leakage	Ensure that membrane is installed properly
	Incorrect internal filling solution	Refill outer body of electrode using filling solution shipped with electrode
	Total level of dissolved species above 1M	Dilute solution
	Electrode in sample too long; NH_3 loss	Reduce surface-area-to-volume ratio, slow rate of stirring, avoid high temperatures
	Membrane failure (wet, perforation, discoloration)	Replace membrane
	Solutions not at constant temperature	Allow solutions to come to room temperature before use
	Heat generated by Magnetic stirrer	Place insulating material between stirrer and beaker
	Defective inner body	Check inner body operation
	Electrode exposed to air for extended period	Hold electrode by outer body and pull up on electrode cable. Interal filling solution will flow under membrane and restore electrode response.
	Samples and standards at different temperatures	Allow solutions to come to room temperature before measurement

PROBLEM	MOST LIKELY CAUSE	SOLUTION
Low slope or No slope	Standards contaminated or incorrectly made	Prepare fresh standards
	ISA not used	Used recommended ISA, Orion Cat. No 951211
	Standard used as ISA	Use ISA!
	Electrode exposed to air for extended period	Hold electrode by outer body and pull up on electrode cable. Interal filling solution will flow under membrane and restore electrode response.
	Membrane failure (wet, perforation, discoloration)	Replace membrane
	Defective inner body	Check inner body operation
"Wrong Answer" (But calibration curve is OK)	Incorrect scaling of semilog paper	Plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
	Incorrect sign	Be sure to note sign of millivolt value correctly
	Incorrect standards	Prepare fresh standards
	Wrong units used	Apply correct conversion factor: 10^{-3}M = 17 ppm as NH_3 = 14 ppm as N
	Complexing agents in sample	Use known addition or titration techniques, or a decomplexing procedure
	ISA added to standards and not samples	Add same proportion of ISA to standards and samples

PROBLEM	MOST LIKELY CAUSE	SOLUTION
Frequent build-up of deposits on ammonia probe membrane	Precipitation of hydroxides from sample	Add EDTA (Ethylene dramine tetraacetic acid) to the NaOH-NaI solution

Quality Control for Total Kjeldahl Nitrogen

Document the Following:

- Supply Water Quality Conductivity
  Ammonia Free
- **ALL** reagents must be made with ammonia free distilled water.

Sampling

- Sample Type
- Sample Time
- Duration of Composite
- Type of Composite
  - Time/Flow - include discrete volumes
  - Flow - include sample volume/discharge volume
  - Straight - document <10% flow rate change during sampling event
- Sample Location
- Preservation - H_2SO_4 <pH2 (2mL/Liter)
  - Volume of H_2SO_4 used
  - Refrigerate at 4°C
  - Hold Time - The maximum allowable hold time if properly preserved and refrigerated is 28 days. However, the sample should be analyzed as soon as possible due to conversion of organic nitrogen to ammonia.

Glassware

- Acid washed - Distilled water rinses - Class A

Equipment

- Distillation Apparatus: Properly "steamed out" before each use.
  Properly cleaned between samples

Analytical Results

- Blank - Treated just as sample result
- Standards - Treated just as sample. Number and concentrations used.
- Preparation Method results
- Standard Curve

Reporting Total Kjeldahl Nitrogen Data

TKN Bench Sheet
Sample Type:
Sampling Time & Date:
Sample Volume:
Sample Preservation:
Analyst:
Analysis Time and Date:
Method:
Blank Result:
Standards:
Concentrations Used:
Standard Curve:
Results of Individual Standards:
Sample Results:
Raw Data (millivolt readings):
Plotted Results on Curve:
Calculations:

Sample TKN Data Sheet

Date: 06-21-2021
Analyst: A D F
Probe Slope Check: -57.2 MV

TKN Report Sheet

	Lab ID	mL Sample	MV	Conc (mg/l)	COMMENTS
1	Blank	50 DI Water	-9.1	0.054	
2	Standard 0.2	1 mL 0.01 mg/l	-40.1	.186	Back Calculations
3	Standard 0.4	2 mL 0.01 mg/l	-62.9	.463	corr = .994
4	Standard 1.0	5 mL 0.01 mg/l	-80.5	.935	
5	Standard 4.0	20 mL 0.01 mg/l	-116.7	3.968	
6	QC TV 4.8	25	-105.0	4.92	% Bias= $\frac{4.92-4.80}{4.80}$ = +2.5%
7	12345	50	-43.1	0.16 <DL	
8	12341	2	-83.7	26.5	%RPD= $\frac{28.4-26.5}{27.5}$= $\frac{1.9}{27.5}$ =6.9%
9	12341 Dup	2	-85.4	28.4	
10	12342	25	-103.2	4.57	%Rec= $\frac{(0.54)(53)-<DL}{3(10)}$=95.4%
11	12343	50	-64.2	0.43	
12	12344	25	-111.3	6.34	
13	12346	50	-105.1	2.44	
14	Spike 12345	50 + 3	-70.5	0.54	3 mL 10 mg/l spike
15					

References

The selective ion electrode method for the determination of Total Kjeldahl Nitrogen can be found in section 4500-N in the 23rd Edition of Standard Methods for the Examination of Water and Wastewater -

and in EPA's Methods for Chemical Analysis of Water and Wastes. Method 351.4 Storet No .00625

The troubleshooting section can be found in the Orion Model 95-12 Ammonia Electrode Instruction Manual

Appendix I: Total Kjeldahl Nitrogen Distillation

Reagents

- NaOH - THIOSULFATE SOLUTION: 500 g NaOH, 25 g $Na_2S_2O_3.5H_2O$ in 1 liter D.I. water.
- SULFURIC ACID: 0.1 mL concentrated H_2SO_4 to 10 mL D.I. water in each 50 mL volumetric used to collect distillate.

Glassware Preparation

- Steam out distillation apparatus before use.
- Label 50 mL volumetric receiving flasks for all blanks standard and samples.
- Add sulfuric acid described in reagent section to each flask.
- Condenser temp. must be below 29°C.

Procedure

1) Quantitatively transfer digested sample, standard, or blank into distilling unit. Use D.I. water to make the total volume about 30 mL.
2) Add 10 mL NaOH - thiosulfate reagent.
3) Close both stopcocks and turn rheostat up to 110 to do distillation. Be sure deliver tube is below surface of sulfuric acid in receiving flask.
4) At end of distillation raise delivery tube out of liquid, then turn rheostat down to 30.
5) Open both stopcocks and drain chamber.
6) Rinse several times with D.I. water.
7) With both stopcocks open and stream off (at 30) add sample and reagent.
8) Lower delivery tube below liquid, close stopcocks and turn up to 110 for next distillation.
9) Do 2 distillation blanks at beginning and one after each high sample.
10) Bring distillates up to 50 mL volume with D.I. water.
11) Cover with parafilm and continue with analysis by phenate method or by ammonia probe (see procedure section).

Reference

Standard Methods for the Examination of Water and Wastewater, 23rd Edition, Method 4500- NH_3B