| UNIVERSITY OF KWAZULU-NATAL | *Standard Operating Procedure* PRG pollution research group | **Effective Date:** 14 April 2015 | **Version:** ***003*** |
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| **SOP_Chem_009 Chemical Analysis_ Free Saline Ammonia** | | | Page #: ***1 of 6*** |

# Standard Operation Procedure – Nitrogen, Ammonia ($NH_3$-N)

## 1. Scope and Application

- Ammonia is naturally present in surface and wastewaters.
- It is produced largely by the deamination of waters and wastewaters. The forms of nitrogen of the greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia and organic nitrogen.
- All these forms of nitrogen as well as nitrogen gas are biochemically inter-convertible and are components of the nitrogen cycle.
- The method covers the range from about 10 to 25mg/L for titrimetric procedure.

## 2. Summary

- The sample is buffered at pH 9.5 with a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds.
- It is distilled into a solution of boric acid when titration is to be used.
- The ammonia in the distillate is determined titrimetrically with standard sulphuric acid and a mixed
- indicator together with a pH meter.

## 3. Apparatus and Glassware

- VELP Distillation unit
- HANNA pH meter
- Analytical balance
- Porcelain or aluminium crucibles, 50ml
- Distillation flasks, 300ml
- Conical flasks, 250ml
- Auto-burette

## 4. Interferences

- Glycine, urea, glutamic acid, cyanates and acetamide hydrolyze very slowly in solution on standing but of these only urea and cyanates hydrolyze on distillation at pH 9.5.

## 5. Collection, Preservation and Storage

- Collect samples in 1L plastic buckets.
- Preferably, analyze samples immediately after sampling.
- Store samples at 4 °C or freeze dry samples.
- Preserve wastewater samples by acidifying with concentrated sulphuric acid to pH 2 and faecal samples by freeze drying or freezing.
- Determine COD on well- homogenized samples.

## 6. Safety Precautions

- Handle concentrated sulphuric acid with care.
- Always use safety goggles, gloves and laboratory coat while working in laboratory.
- Wear face shield and protect hands from heat produced when contents of the vessels are mixed.
- After the analysis, clean bottles and beakers with water then dry.
- Dispose used gloves after completion of analysis.
- Clean hands using antiseptic soap.
- Avoid spillage and contact with skin. In the latter case use copious washings with cold water and call for medical attention.

## 7. Sample Preparation –Faecal Sludge

1. Weigh out 2.0000g of well-mixed faecal sludge sample.
2. Blend the weighed sample with 500ml of distilled water in a 1L blender for 30 seconds on the highest speed.
3. Add 250ml distilled water and blend on highest speed until the sample is homogenized (this could range from 30 to 60 seconds).
4. Transfer the blended mixture into a 1L volumetric flask.
5. Add 200ml of blender washings into the flask and top up to 1L with distilled water.
6. Transfer the 1L solution to a plastic bottle and store at 4 °C.

## 8. Reagents

**Ammonia Free Water**

- Eliminate traces of ammonia in distilled water by adding 0.1ml sulphuric acid to 1L distilled water and redistill. Alternately, treat distilled water with enough bromine or chlorine water to produce a free halogen residue of 2-5 mg/L and redistill after standing for 1 hour.

**0.1N NaOH**

Dissolve 4g NaOH in 1L distilled water.

**1N NaOH**

- Dissolve 40g NaOH in 1 ammonia free distilled water.

**Borate Buffer Solution**

- Add 88mL of 0.1N NaOH solution to 500ml of 0.025M di-sodium tetra borate-hydrous ($Na_2B_4O_7$. $10H_2O$) solution – (9.5g $Na_2B_4O_7$. $10H_2O$ hydrous per liter) or (5.0g $Na_2B_4O_7$ anhydrous per liter) and dilute to 1L.

**Mixed indicator Solution**

- Dissolve 200mg methyl red indicator in 100ml 95% ethyl or isopropyl alcohol or ethanol. Dissolve 100mg methylene blue in 50ml 95% ethyl or isopropyl alcohol or ethanol. Combine solutions. Prepare monthly.

**Indicating Boric acid Solution**

- Dissolve 20g $H_3BO_3$ in ammonia free distilled water, add 10ml mixed indicator solution and dilute to 1L.
- Prepare monthly.

## 9. Calibration

- To calibrate test solutions of 5.0, 10, 50 and 100 mg/l $NH_4$-N.
- Prepare a series of at least three standards, covering the desired range, and a blank by diluting suitable volumes of standard solutions. Prepare a calibration curve by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor. Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and re-analyzed. Report results in mg/L.

**Standard Sulphuric acid Titrant, 0.02N**

- Dissolve 0.5ml conc sulphuric acid in distilled water and dilute to 1litre.
- Weigh out about 1.325g anhydrous Sodium Carbonate, previously dried at 270°C. Dissolve in distilled water and make up to 250ml in a volumetric flask- this is 0.10N. Do not keep longer than 1 week.
- Titrate the sulphuric acid solution against 25ml of sodium carbonate solution using bromocresol green-methyl red mixed indicator. Calculate the normality of the sulphuric acid.

$$Normailty\ of\ H_2SO_4\ Solution = \frac{25 \times 0.1}{Vol\ \ H_2SO_4\ used}$$

**Quality control:**

- Ammonium chloride, stock solution: 1.0mL=1.0mg NH3-N.
- Dissolve 3.819g NH4Cl in distilled water and bring volume to 1L with distilled water in a volumetric flask.
- Ammonium chloride, STD solution: 1.0mL = 0.01mg.
- Dilute 10mL of stock solution to 1 litre in a volumetric flask to give a conc of 10mg/L $NH_3$-N.

## 10. Procedure

### Preparation of Equipment

Add 500ml ammonia – free water and 20 ml borate buffer to a distillation flask and adjust pH to 9.5 with 6N NaOH solution. Add a few glass beads and use this mixture to steam out the distillation apparatus until distillate shows no traces of ammonia.

| Ammonia Nitrogen In Sample Mg/L | Sample Volume mL |
|---|---|
| 5-10 | 250 |
| 10-20 | 100 |
| 20-50 | 50.0 |
| 50-100 | 25.0 |

- Add 70ml of sample to distillation flask.
- Add 20ml borate buffer to distillation flask.
- Distill for 5min and collect 100ml distillate into the 50 ml indicating boric acid solution.
- Titrate ammonia in distillate with standard 0.02N sulphuric acid; titrate until indicator turns a pale lavender.
- Carry a blank through all steps of the procedure and apply the necessary correction to the results.

## 11. Waste Disposal

- Collect waste in a 2.5L bottle for Waste Tech collection.

## 12. Calculation and Data Analysis

$$NH_3 - N\ (mg/L) = \frac{(A - B) \times 280}{Sample\ (ml)}$$

Where:
A = volume of $H_2SO_4$, titrated for sample, ml
B = Volume of $H_2SO_4$, titrated for blank, ml
Sulphuric acid: Standard solution (0.02N, 1mL=0.28mg NH3-N) 1L-280mg NH3- N

Concentration = mass/Molar mass

$$NH_3 - N\ in\ Wet\ Sample\ (mg/g) = \frac{(A-B)\times 280}{Sample\ (ml)} \times \frac{V}{M}$$

$$NH_3 - N\ in\ Wet\ Sample\ (g/g) = \frac{NH_3\ in\ Wet\ Sample\ (mg/g)}{1000}$$

$$NH_3 - N\ in\ Dry\ Sample\ (g/g) = \frac{NH_3\ in\ Wet\ Sample\ (g/g)}{Total\ Solids\ (g/g)}$$

Where:
M = Mass of sludge used in sample preparation (g)
V = Volume of dilution (L)

## 13. Data Quality

| | |
|---|---|
| Measurement | 10 – 150 mg/ |
| Standard Deviation (mg/l COD) | |
| Confidence Interval (mg/l COD) | |
| Sensitivity (mg/l COD) | |
| Accuracy (mg/l COD) | |

## 14. References


- Standards Methods for the Examination of Water and Wastewater, 18th Edition, p. 4-110/112, Methods 4500 NH3 B and C Preliminary Distillation Step and Titrimetric Method (1992).


## APPROVAL OF STANDARD OPERATING PROCEDURE

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