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| **METHOD #: 351.4** | Pending Approval for NPDES (Issued 1978) |
| **TITLE:** | Nitrogen, Kjeldahl, Total (Potentiometric, Ion Selective Electrode) |
| **ANALYTE:** | CAS # N Nitrogen 7727-37-9 |
| **INSTRUMENTATION:** | ISE |
| **STORET No.** | 00625 |

1.0 Scope and Application

1.1 This method is applicable to the measurement of TKN in drinking and surface water, domestic and industrial wastes.
1.2 This method covers the range from 0.03 to 25 mg TKN/L.

2.0 Summary of Method

2.1 Following digestion and cooling, distilled water is added to the digestion flask and the pH adjusted to between 3 and 4.5 by the addition of 10 N NaOH. The sample is cooled and transferred to a 100 mL beaker. After inserting the electrode into the sample, NaOH-NaI-EDTA is added and the ammonia measured. (Ethylene diamine tetraacetic acid (EDTA) is added to the alkaline reagent (NaOH-NaI) to prevent precipitation of hydroxides, thereby avoiding deposition on the electrode membrane).

3.0 Sample Handling and Preservation

3.1 Samples may be preserved by addition of 2 mL of conc. $H_2SO_4$ per liter and stored at 4°C. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.

4.0 Interferences

4.1 Interference from metals is eliminated with the addition of NaI.
4.2 High nitrate concentrations (1OX or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

5.0 Apparatus

5.1 Electrometer (pH meter) with expanded mV scale.
5.2 Ammonia selective electrode, such as Orion Model 95-10.
5.3 Magnetic stirrer, thermally insulated and Teflon-coated stirring bar.
5.4 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 mL flasks

and suction take off to remove $SO_3$ fumes and water.

5.5 Technicon Block Digester BD-40.

6.0 Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passing distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

6.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide (HgO) in 50 mL of 1:4 sulfuric acid (10.0 mL conc $H_2SO_4$: 40 mL distilled water) and dilute to 100 mL with distilled water.

6.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g $K_2SO_4$ in 1300 mL distilled water and 400 mL conc $H_2SO_4$. Add 50 mL mercuric sulfate solution (6.2) and dilute to 2 liters with distilled water.

6.4 Sodium hydroxide 1O N: Dissolve 400 g NaOH in 600 mL of ammonia-free water, cool and dilute to 1 liter.

6.5 Sodium Hydroxide, Sodium Iodide and EDTA Solution: Dissolve 400 g of NaOH, 300 g - NaI and 2 g of EDTA in 700 mL of ammonia-free water, cool and dilute to 1 liter.

6.6 Ammonium chloride, stock solution: 1.0 mL = 1.0 mg $NH_3$-N. Dissolve 3.819 g $NH_4Cl$ in water and make up to 1 liter in a volumetric flask with distilled water.

6.7 Ammonium chloride, standard solution: 1.0 mL = 0.01 mg $NH_3$-N. Dilute 10.0 mL of the stock solution (6.6) to 1 liter with distilled water in a volumetric flask.

7.0 Procedure

7.1 Macro Kjeldahl system

7.7.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 mL Kjeldahl flask. The sample size can be determined from following table:

| Kjeldahl Nitrogen in Sample, mg/L | Sample Size mL |
|---|---|
| 0-5 | 500 |
| 5-10 | 250 |
| 10-20 | 100 |
| 20-50 | 50.0 |
| 50-500 | 25.0 |

Dilute the sample, if required, to 500 mL with distilled water and add 100 mL sulfuric acid-mercuric sulfate-potassium solution (6.3) and evaporate the mixture in the Kjeldahl apparatus until $SO_3$ fumes are given off and the solution colorless or pale yellow. Continue heating for 30 minutes. Cool the residue and add 500 mL distilled water and mix.

7.2 Micro Kjeldahl system

7.2.1 Place 50.0 mL of sample, or an aliquot diluted to 50 ml, in a 100 mL Kjeldahl flask and add 10 mL sulfuric sulfate-potassium sulfate solution (6.3). Evaporate the in the Kjeldahl apparatus until $SO_3$ fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue, add 44 mL distilled water and mix.

7.3 Block Digester

7.3.1 Place 20 mL of sample, or an aliquot diluted to 20 ml, in digestion tube. Add 5 mL of sulfuric acid-mercuric sulfate-potassium sulfate solution (6.3) and mix. Add 4-8 Teflon boiling stones.

7.3.2 Place tubes in digester that has been preheated to 200°C.

7.3.3 Set low temperature at 200°C for 1 hour, the high temperature 380°C and total time for two and one half hours.

7.3.4 After the temperature of the block has reached 380°C, the time should be set for 30 minutes. Longer time and higher temperature may result in complete loss of the acid.

7.3.5 Cool, add 25 mL of ammonia-free water and mix.

7.4 Electrode analysis

7.4.1 All standards should be treated as the samples and should contain the same concentration of sulfuric sulfate-potassium sulfate solution (6.3).

7.4.2 Macro Kjeldahl system

To a 100 mL aliquot, add 15 mL of 10 N NaOH (6.4), mix and cool to room temperature. Immerse the electrode in the sample solution and add 4 mL of NaOH-NaI-EDTA reagent (6.5) while mixing. The electrode to remain immersed in the solution until a stable reading is obtained.

7.4.3 Micro Kjeldahl system

Add 6 mL of 10 N NaOH solution (6.4), cool to room temperature and transfer the sample to a 100 mL beaker. Immerse the electrode in the sample solution and add 4 mL of NaOH-NaI-EDTA reagent (6.5) while mixing. Allow the electrode to remain immersed in the solution until a stable reading is obtained.

7.4.4 Block Digester

Add 3 mL of 10 N NaOH (6.4), cool to room temperature, dilute to 50 mL and transfer to a 100 mL beaker. Immerse the electrode the sample and add 2 mL of NaOH-NaI-EDTA reagent (6.5) while mixing. Allow the electrode to remain immersed in the solution until a stable reading is obtained.

8.0 Calculation: Using semilogarithmic graph paper, plot the concentration of ammonia in mg $NH_3$-N on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.

$$mg\ \text{TKN/L} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = mg $NH_3$-N read from standard curve
B = mg $NH_3$-N in blank
C = mL of original sample taken

9.0 Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

## Bibliography

1. Schlueter, A., "Nitrate Interference in Total Kjeldahl Nitrogen Determinations and its Removal by Anion Exchange Resin", EPA-600/7-77-017.