Technical Bulletin

# Nitrate Measurements in Environmental Samples

## Introduction

The Thermo Scientific Orion nitrate test kit, Cat. No. 700005, can be used for nitrate measurements in a wide variety of samples, such as natural waters, drinking waters, soils and fertilizers. The method is free from the interferences encountered in most other nitrate measurement techniques. Traditional colorimetric and spectrophotometric methods encounter interferences due to sample color and turbidity. While analysis can be made using a nitrate ion selective electrode, suppression of interferences, particularly chloride and carbonate, is usually necessary and sometimes unsuccessful. The nitrate test kit solves these problems and is easy to use.

The kit uses an ammonia electrode for measurement and takes advantage of some simple chemistries. Standards and samples are both made basic with the addition of an alkaline reagent, and then a reducing agent containing titanous chloride is added. Nitrate is converted to ammonia under these conditions and is then measured with the ammonia electrode. Ions that interfere with the nitrate electrode, such as chloride, have no effect on the measurement. Samples containing 0.1 to 20 ppm of nitrate-nitrogen can be analyzed directly with the kit. Higher sample concentrations can be diluted before measurement. If ammonia is present in the samples and its concentration is significant relative to the nitrate concentration, the ammonia concentration must be measured separately and subtracted from the nitrate results.

## Required Equipment

- An ISE meter with a direct concentration readout is the easiest to use. If this type of meter is unavailable, a pH/mV meter with a 0.1 mV resolution is recommended.
- High performance ammonia electrode, Cat. No. 9512HPBNWP.
- Magnetic stirrer or Thermo Scientific Orion stirrer probe, Cat. No. 096019. The Orion stirrer probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.
- Volumetric flasks, graduated cylinders and beakers.
- Nitrate test kit for 100 tests, Cat. No. 700005, includes 2 x 50 mL bottles of ammonia electrode filling solution, Cat. No. 951203; 475 mL bottle of 100 ppm ammonia as nitrogen standard, Cat. No. 951207; 475 mL bottle of 100 ppm nitrate as nitrogen standard, Cat. No. 930707; 475 mL bottle of reducing agent, Cat. No. 700006; and 2 x 475 mL bottles of alkaline reagent, Cat. No. 951011;
- Distilled or deionized water, to dilute all samples and standards.

## Setup

1. Prepare the meter according to the directions in the meter user guide.
2. Condition and assemble the ammonia electrode according to the electrode user guide and fill the electrode with the ammonia electrode filling solution that is included with the test kit, Cat. No. 951203, instead of the one normally supplied with the electrode.
3. Connect the ammonia electrode to the meter.
4. Verify the ammonia electrode slope according to the Checking Electrode Operation (Slope) procedure in the ammonia electrode user guide. Use the 100 ppm ammonia standard provided in the kit.

## Calibration

1. Prepare two calibration standards, 10 ppm and 1 ppm nitrate as nitrogen ($NO_3$ as N), by serially diluting the 100 ppm $NO_3$ as N standard that is included in the test kit. To prepare the 10 ppm standard, add 25 mL of the 100 ppm standard to a 250 mL volumetric flask and dilute to the mark with distilled water. To prepare the 1 ppm standard, add 25 mL of the 10 ppm standard to a 250 mL volumetric flask and dilute to the mark with distilled water. Place 100 mL of each standard into separate beakers and label the beakers.

2. Rinse the electrode, place it in the 1 ppm standard, and stir the solution moderately using a magnetic stirrer or stirrer probe. Add 10 mL of the alkaline reagent, Cat. No. 951011, followed by 2 mL of the reducing agent, Cat. No. 700006. When the reading is stable, after approximately 2 minutes, set the meter to read 1 ppm or record electrode potential in mV.

3. Rinse the electrode, place it in the 10 ppm standard, and stir the solution moderately using a magnetic stirrer or stirrer probe. Add 10 mL of the alkaline reagent, followed by 2 mL of the reducing agent. When the reading is stable, after approximately 2 minutes, set the meter to read 10 ppm or record electrode potential in mV. The slope should be about 47 mV or greater. Due to ionic strength differences, it is normal to obtain slopes between 47 and 57 mV/decade.

4. Set the meter to the measurement mode or prepare a calibration curve by plotting, on semi-logarithmic graph paper, the millivolt readings observed (linear axis) versus the concentrations (log axis) of the 1 and 10 ppm standards.

## Measurements

1. Add 100 mL of sample to a 150 mL beaker and prepare the sample as directed in **Table A** or **Table B**. Add 10 mL of alkaline reagent followed by 2 mL of reducing agent.

2. Rinse the electrode, place it in the sample, and stir the solution moderately using a magnetic stirrer or stirrer probe. When the reading is stable, approximately 2 minutes, read the nitrate as nitrogen concentration directly from the meter or determine it from the calibration curve. Refer to **Table A** or **Table B** for the correct calculation of nitrate as nitrogen levels based on the sample preparation.

## Measuring Hints

The level of reagents in the kit will convert only a specific amount of nitrate to ammonia. If the sample value you read from the meter or calibration curve is above 20 ppm nitrate as nitrogen, refer to **Table A** or **Table B**, prepare a new sample that is tenfold more dilute than the one currently measured, and repeat the measurement. Additional dilutions may be necessary to adjust sample values to fall within the ideal 1 to 10 ppm calibration range of the test kit.

To insure complete conversion of nitrate to ammonia, an excess of reducing agent should be present. If all reducing agent was used in the conversion, the solution will turn white, indicating the sample should be more dilute. Prepare a more dilute sample and repeat the measurement.

Alkaline reagent must be added first to standards and samples before adding reducing agent. Reagent volumes must be the same for both samples and standards. Both reagents are corrosive chemicals and must be handled with care. Mixing of the reagents will cause a dark black precipitate in standards and samples.

For a large number of samples, prepare samples with reagents in sealed containers and store until measured. Do not use parafilm or other plastic film to seal containers as it is permeable to some gasses.

Nitrite, if present in the sample, is measured with nitrate. If its concentration is significant relative to the nitrate concentration, it can be eliminated by addition of 1 gram of sulfamic acid to the sample and pH adjustment to pH 3 to 4 with HCl before the reagents are added.

**Table A – Waters**

| Expected Levels ($NO_3$ as N) | Sample Preparation[b] | Calculation of Results[c] |
|---|---|---|
| Unknown | Use 100 mL of sample | None required |
| Less than 1 ppm[a] | Use 100 mL of sample | None required |
| 1 to 10 ppm | Use 100 mL of sample | None required |
| 10 to 100 ppm | Dilute 10 mL of sample to 100 mL with distilled water | Value times 10 |
| 100 to 1000 ppm | Dilute 1 mL of sample to 100 mL with distilled water | Value times 100 |
| 1000 to 10,000 ppm | Dilute 1 mL of sample to 1000 mL with distilled water | Value times 1000 |

**Table B – Soils/Fertilizers**

| Expected Levels ($NO_3$ as N) | Sample Preparation[b] | Calculation of Results[c] |
|---|---|---|
| Unknown | Add 1 gram of sample to 100 mL of water. Use 100 mL of prepared sample. | ppm = value x 100% = value x 0.01 |
| Less than 1 ppm or less than 0.01%[a] | Add 10 grams of sample to 100 mL of water. Use 100 mL of prepared sample. | ppm = value x 10% = value x 0.001 |
| 1 to 10 ppm or 0.01 to 0.1% | Add 1 gram of sample to 100 mL of water. Use 100 mL of prepared sample. | ppm = value x 100% = value x 0.01 |
| 10 to 100 ppm or 0.1 to 1% | Add 1 gram of sample to 100 mL of water. Dilute 10 mL of prepared sample to 100 mL. | ppm = value x 1000% = value x 0.1 |
| 100 to 1000 ppm or 1 to 10% | Add 1 gram of sample to 100 mL of water. Dilute 1 mL of prepared sample to 100 mL | ppm = value x 10,000% = value x 0.1 |
| 1000 to 10,000 ppm or 10 to 100% | Add 1 gram of sample to 100 mL of water. Dilute 1 mL of prepared sample to 1000 mL. | ppm = value x 100,000% = value x 10 |

a. For concentrations less than 1 ppm or 0.01%, prepare dilute calibration standards of 0.1 ppm and 1 ppm instead of those suggested.

b. Use only distilled or deionized water for any sample preparation or dilution.

c. To convert ppm or percent $NO_3$ as N to ppm or percent $NO_3$, multiply by 4.43.

## Calibration and Measurement with Ammonia in Samples

Use this procedure when ammonia concentration is significant relative to nitrate concentration (more than 5% of the sample). Containers that can be sealed are required for this procedure.

1. Prepare the meter and the electrodes according to the **Setup** section.

2. Verify the ammonia electrode slope according to the Checking Electrode Operation (Slope) procedure in the ammonia electrode user guide. Use the 100 ppm ammonia standard provided in the kit.

3. Prepare two calibration standards that bracket the expected sample concentrations. Dilute the 100 ppm ammonia standard that is included in the kit to obtain the necessary standards.

4. Rinse the ammonia electrode, place it in the less concentrated ammonia standard, and moderately stir the solution. Add 10 mL of alkaline reagent. When the reading is stable, set the meter to read the standard value or record electrode potential in mV.

5. Rinse the ammonia electrode, place it in the more concentrated ammonia standard, and moderately stir the solution. Add 10 mL of alkaline reagent. When the reading is stable, set the meter to read the standard value or record electrode potential in mV.

6. Set the meter to the measurement mode or prepare a calibration curve by plotting, on semi-logarithmic graph paper, the millivolt readings observed (linear axis) versus the concentrations (log axis) of the standards.

7. Prepare samples according to **Table A** or **Table B**.

8. Place the electrode in the sample and moderately stir the solution. Add 10 mL of alkaline reagent to the sample. When the reading is stable, record the ammonia concentration directly from meter or determine it from the prepared calibration curve.

9. Seal the sample in an airtight container such as glass stopper flask or bottle. Do not use plastic film for sealing containers.

10. After the ammonia concentration has been determined for all samples, recalibrate the electrode for nitrate determination. Prepare a 1 ppm and 10 ppm nitrate standard from the 100 ppm nitrate as nitrogen standard using serial dilution. Refer to the **Calibration** section for instructions.

11. Rinse the electrode, place it in the 1 ppm standard, and stir the solution moderately. Add 10 mL of the alkaline reagent, followed by 2 mL of the reducing agent. When the reading is stable, set the meter to read 1 ppm or record electrode potential in mV.

12. Rinse the electrode, place it in the 10 ppm standard, and stir the solution moderately. Add 10 mL of the alkaline reagent, followed by 2 mL of the reducing agent. When the reading is stable, set the meter to read 10 ppm or record electrode potential in mV.

13. Set the meter to the measurement mode or prepare a calibration curve by plotting, on semi-logarithmic graph paper, the millivolt readings observed (linear axis) versus the concentrations (log axis) of the 1 and 10 ppm standards.

14. Rinse the electrode and place it in first sample. Add 2 mL of reducing reagent and stir the solution. When the reading is stable, read the concentration directly from the meter or record the mV value and determine concentration from the prepared calibration curve.

15. Repeat step 14 for all remaining samples.

16. Subtract the ammonia concentration from the nitrate concentration to obtain the final nitrate concentration for each sample.

## Chemistry

The chemical conversion of nitrate to ammonia when alkaline and reducing reagents are added to samples and standards is as follows:

$$NO_3^- + 8TiCl_3 + 24NaOH \longrightarrow NH_3 + 8TiO_2 + 24NaCl + OH^- + 10H_2O$$

It is imperative that the alkaline reagent be added first as the reaction will only take place under basic conditions.

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