**Method Abstract**

**Scope**
This method is used for the determination of nitrate ($\text{NO}_3^-$) plus nitrite ($\text{NO}_2^-$) or nitrite singly in drinking water, groundwater, surface water, and domestic and industrial wastes according to USEPA Method 353.2 and Standard Methods 4500–$\text{NO}_3^-$ F. Additionally, this method enables nitrate plus nitrite according to ISO Method 13395. Also, this method can be used to analyze nitrate plus nitrite in 2M potassium chloride ($\text{KCl}$) extracts of soils and plants.

**Summary**
Cadmium metal reduces nitrate quantitatively to nitrite. Nydahl provides a good discussion of nitrate reduction by cadmium metal. The nitrite formed, in addition to any nitrite originally present in the sample, is diazotized with sulfanilamide and is subsequently coupled with $N$-$(1$-naphthyl)ethylenediamine dihydrochloride. The resulting highly colored azo dye is colorimetrically detected at 540 nm. A calibration curve allows accurate quantitation of the detected nitrite.

Measure nitrite singly by performing the same analysis as in described before but without cadmium reduction; without cadmium, nitrate is not reduced to nitrite and is not detected since only nitrite forms the azo dye.

**Interferences**
Turbid samples may interfere with the photometric detector’s ability to measure the true absorbance of the sample. Filter turbid samples prior to analysis.

Iron, copper, and other metals may interfere with the analysis by binding with the nitrate and/or nitrite in the sample, thus blocking the color formation reaction. Use of EDTA or other complexing agents in the buffering solution manages this interference.

Samples that are outside the functional pH range of the buffering solution may affect the results obtained from this method. Adjust the pH of these samples to within a range of 5-9 using either concentrated hydrochloric acid (HCl) or sodium hydroxide (NaOH).

Oil and grease will coat the cadmium surface, thus reducing its reduction efficiency. Extract samples containing large concentrations of oil and grease with an appropriate organic solvent.

Sulfide in the presence of cadmium will form cadmium sulfide (CdS), which will inhibit nitrate reduction. Samples containing sulfide cannot be determined using this method without first removing the sulfide by precipitation with cadmium salts.

Dissolved oxygen and carbonate can react with the cadmium to form cadmium hydroxide ($\text{Cd(OH)}_2$) and cadmium carbonate ($\text{CdCO}_3$) precipitants. Additionally, dissolved oxygen competitively inhibits the reduction of nitrate to nitrite. Care must be taken to ensure that the pH never exceeds 8.5. Also, degas all reagents prior to analysis.

Chlorine may reduce the reduction efficiency of the cadmium reactor. Samples that may contain residual chlorine should be tested for reduction efficiency through the analysis of Matrix Spike/Matrix Spike Duplicate (MS/MSD) samples (Section 9.3). When necessary, dechlorinate samples with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$).

Method interferences may be caused by contaminants in the reagents, reagent water, glassware, etc., which may bias the results. Care should be taken to keep all such items free of contaminants.
Norwitz and Keliher, as well as Nydahl, have compiled a comprehensive study of interferences in the spectrophotometric analysis of nitrite.

**Performance Specifications**

- **Range:** 0.005–10.0 mg/L
- **Throughput:** 55 samples/hour
- **Precision (at 0.01 mg/L):** ~4% RSD
- **Precision (at 0.1 mg/L):** <0.5% RSD
- **Precision (at 1.0 mg/L):** <1% RSD
- **Precision (at 10.0 mg/L):** <0.5% RSD
- **Method Detection Limit (MDL):** 0.0005 mg/L
- **Accuracy:** 108.88%
- **Cadmium Coil Reduction Efficiency:** 96.03%

**Chemicals**

- Ammonium Chloride (low nitrate), NH₄Cl
- Ammonium Hydroxide, NH₄OH
- Brij®-35, 21% solution (part number A21-0110-33)
- Chloroform, HPLC Grade, CHCl₃
- Cupric Sulfate Pentahydrate, CuSO₄•5H₂O
- Deionized (DI) Water, ASTM Type I or II
- Ethylenediaminetetraacetic Acid, Disodium Salt Dihydrate (EDTA), C₁₀H₁₆N₂Na₂O₈•2H₂O
- Hydrochloric Acid, concentrated, HCl
- Imidazole, C₃H₄N₂
- N-(1-naphthyl)ethylenediamine dihydrochloride, C₁₂H₁₄N₂•2HCl
- Phosphoric Acid, concentrated, H₃PO₄
- Potassium Nitrate, KNO₃
- Potassium Nitrate, KNO₂
- Sulfanilamide, C₆H₈N₂O₂S

**Basic Flow Diagram**

```
Working Buffer
Nitrogen
Sample
Color Reagent

24" Open Tubular Cadmium Reactor (OTCR)
Debubbler
540 nm
To Waste
```

**Selected Reference**

*Methods for the Determination of Inorganic Substances in Environmental Samples; EPA/600/R-93/100; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1993; Method 353.2.*


**Figures**

![Figure 1. Nitrate Calibration (0.005–10.0 ppm)](image-url)
Nitrate plus Nitrite Nitrogen and Nitrite Nitrogen, USEPA by SFA

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Figure 2. Nitrite Nitrogen Calibration (0.005–10.0 ppm)

Figure 3. Nitrate Calibration Curve (0.005–10.0 ppm)
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Figure 4. Nitrite Nitrogen Calibration Curve (0.005–10.0 ppm)

Figure 5. Nitrate Method Detection Limit (at 0.005 ppm)
Figure 6. Nitrite Nitrogen Method Detection Limit (at 0.005 ppm)

Figure 7. Nitrate Precision (at 0.01 ppm)
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Figure 10. Nitrate Precision (at 10.0 ppm)

Figure 11. Nitrite Nitrogen Precision (at 0.01 ppm)
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Figure 12. Nitrite Nitrogen Precision (at 0.1 ppm)

Figure 13. Nitrite Nitrogen Precision (at 1.0 ppm)
Figure 14. Nitrite Nitrogen Precision (at 10.0 ppm)

Figure 15. Nitrate plus Nitrite Nitrogen ERA QC Sample Precision (ERA 1.98 ppm)
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Figure 16. Nitrate plus Nitrite Nitrogen ERA QC Sample Precision (2 M KCl extract 1.4 ppm)

Figure 17. Nitrate Calibration Results (0.005–10.0 ppm)
Figure 18. Nitrite Nitrogen Calibration Results (0.005–10.0 ppm)
**Table 1. Nitrate plus Nitrite Nitrogen and Nitrite Nitrogen Method Data**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calibrant 0.005 mg/L</th>
<th>Calibrant 0.01 mg/L</th>
<th>Calibrant 0.1 mg/L</th>
<th>Calibrant 1.0 mg/L</th>
<th>Calibrant 10.0 mg/L</th>
<th>ERA QC Standard 1.98 mg/L</th>
<th>2 M KCl Soil Extract QC Standard 1.4 mg/L</th>
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