# Seawater Nutrient Analysis by Segmented Flow Analysis

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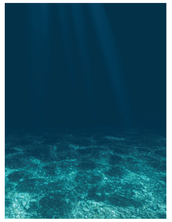
## Section 1. Introduction

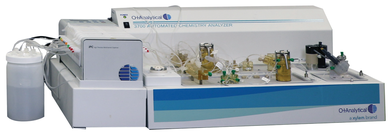


Seawater nutrients play a vital role in oceanic seafood chain. Quantification of these nutrients forms the foundation for understanding oceanic productivity and their analyses can be used to measure and monitor many oceanic cycles. Soluble inorganic nitrogen, phosphorous, and silicate in seawater are essential for the survival of marine organisms. A moderate amount of nutrients in seawater promotes the growth of biology and microorganisms. Inadequate amounts of nutrients restrict the growth of phytoplankton. Excessive nutrient growth is prone to cause eutrophication and lead to harmful algae blooms (HABs), and even the death of aquatic organisms. Excess nutrients in seawater can be attributed to several sources, but the crux of the nutrients in seawater comes from human activities and sources. Fertilizers run off, animal waste, and wastewater processes are the main sources of excess nutrients in seawater.

The U.S. EPA has endorsed several methods to monitor and measure nutrients in seawater. The nutrients of concern are nitrate, nitrite, ammonium, orthophosphate, and silicate. Each of these nutrients present their own challenges. Nitrogen and phosphorous naturally enter estuarine and seawater when freshwater runoffs pass over geological formations rich in nitrogen and phosphorous, or when decomposing organic matter and wildlife waste gets flushed into rivers and streams. Silicate is of interest because of its impact on global $CO_2$ concentrations through the combined processes of weathering of silicate minerals and transfer of $CO_2$ from the atmosphere to the lithosphere. Silicate production can be limited by the availability of dissolved silicate. Plankton construct their exoskeletons from silica. Ammonia nitrogen is found in low concentrations in seawater. Higher levels of ammonia in seawater can be directly and indirectly toxic to many marine organisms. Large scale agricultural, animal waste, and industrial run-offs are significantly increasing ammonia concentrations in seawater and estuaries.

Flow analysis techniques play an important role in water analysis and monitoring. Several flow-based methods have been successfully developed for the photometric determination of the above-mentioned nutrients in brackish or seawater containing up to 3.5% dissolved sodium chloride. A 3.5% sodium chloride solution (by weight) in aqueous solution is often used, approximating the concentration of salt present in seawater. For this study, a 3.6% sodium chloride solution was used as a more aggressive matrix.

This poster will focus on seawater analysis for $NO_3$+$NO_2$, and $NH_3$. SFA (segmented flow analysis) is a flow-based method that has been proven reliable and consistent running the difficult matrix of seawater. It is widely used by chemical oceanographers because it provides the fastest and most precise measurements. This study will demonstrate the accuracy and consistency of the SFA technique using the latest O.I. FS3700 Automated Chemistry Analyzer to generate dependable and practical data for seawater characterization and monitoring.



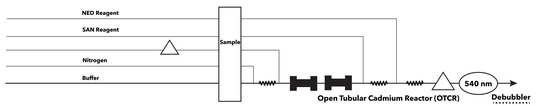

## Section 2. Experimental

The FS3700 system configuration consists of a 3180 autosampler, 24 channel peristaltic pump, analytical cartridge consisting of several mixing tees, a single air segmentation tee and, a photometric detector equipped with 10 mm flowcell. Samples and calibration curve were prepped with a low nutrient seawater solution. A 540 nm wavelength filter was installed on the photometric for NO3/NO2 and NO2 analysis.

### Principle of Operation – Method

This method is used to determine the concentration of nitrate ($NO_3^-$) plus nitrite ($NO_2^-$) or nitrite singly in estuarine and coastal waters (seawater) according to USEPA Method 353.4 (Reference 1). The Method Detection Limit (MDL) of this method is 0.25-µg/L nitrogen (0.018 µmoles/L nitrogen). Theapplicable range of the method is 1.0–5,000 µg/L nitrogen (0.07–357 µmoles/L nitrogen). The range may be extended to analyze higher concentrations by sample dilution. Nitrate is reduced quantitatively to nitrite by cadmium metal. Nydahl (Reference 2) 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 (SAN) and subsequently coupled with N-(1-naphthyl)ethylenediamine dihydrochloride (NED). The resulting highly colored azo dye is colorimetrically detected at 540 nm (Reference 2). A calibration curve allows for accurate quantitation of the detected nitrite. Nitrite singly may be measured by performing the same analysis without the cadmium reduction. Without the cadmium, nitrate is not reduced to nitrite and is not detected since only nitrite forms the azo dye.

**Flow Schematic: General flow diagram of the NO3/NO2 SFA configuration.**




**Method Parameters**

| | | |
|---|---|---|
| Analysis Settings | Mode | SFA |
| | Load Time | 20 seconds |
| | Cycle Duration | 150 seconds |
| Heater Settings | Enable | |
| UV Lamp Settings | Not Used | |
| Detector Settings | Mode | Photometric |
| | Polarity | Normal |

**Signals/Peak Marking**

| | | |
|---|---|---|
| Peak Measurement | Measure Peaks by | Height |
| | Baseline Value for Peak-marking | Sync-Peak Start as Baseline (default) |
| | Apply Carryover Correction to all Samples | No |
| | Minimum Peak Height | 250 |
| | Minimum Peak Width | 50 |
| Smoothing | Moving Average | 5 points |
| Sync Peak Marking | Recognize Peak Start by a rise of | 500 Counts |
| | ... total counts within | 5 seconds |
| | Sync Peak Ignore Time | 60 seconds |
| | Use Return to Baseline | ✓ |
| | Return-to-Baseline % | 99% |
| | Use D1V | ✓ |

These are suggested initial settings. Adjust as necessary for optimal performance.

**Calibration Table**

| Enable | | Target Concentration |
|---|---|---|
| | STD1 | 0 |
| ✓ | STD2 | 1 |
| ✓ | STD3 | 5 |
| ✓ | STD4 | 10 |
| ✓ | STD5 | 50 |
| ✓ | STD6 | 100 |
| ✓ | STD7 | 500 |
| ✓ | STD8 | 1000 |
| ✓ | STD9 | 5000 |
| Calibration Curve Fitting Method | | Weighted LInear |
| Calibrant Units | | µg/L |

**MDL, Precision, and Accuracy Study – $NO_3$/$NO_2^-$**

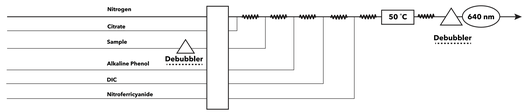
| Parameter $NO_3$ $NO_2$ in Seawater | Calibrant 1.0 µg/L | Calibrant 10.0 µg/L | Calibrant 100.0 µg/L | Calibrant 1000.0 µg/L | ERA QC Standard 8.59 mg/L |
|---|---|---|---|---|---|
| $NO_3/NO_2$ | 1 | 10 | 200 | 1000 | 8.59 |
| Replicate 1 | 0.98 | 9.85 | 98.14 | 1011.79 | 8.54 |
| Replicate 2 | 1.07 | 10.61 | 99.64 | 1001.22 | 8.47 |
| Replicate 3 | 1.11 | 10.20 | 99.82 | 1014.74 | 8.28 |
| Replicate 4 | 0.97 | 10.33 | 100.04 | 971.94 | 8.35 |
| Replicate 5 | 0.94 | 10.32 | 100.04 | 1096.45 | 8.30 |
| Replicate 6 | 1.04 | 10.33 | 99.79 | 980.51 | 8.49 |
| Replicate 7 | 1.09 | 10.49 | 99.86 | 974.79 | 8.45 |
| Replicate 8 | 1.03 | 10.45 | 100.21 | 1006.79 | 8.45 |
| Replicate 9 | – | | 100.02 | 989.85 | 8.36 |
| Replicate 10 | – | | 100.55 | 983.30 | 8.26 |
| Average | 1.04 | 10.32 | 99.81 | 1003.14 | 8.40 |
| Standard Deviation | 0.07 | 0.23 | 0.64 | 36.20 | 0.10 |
| % RSD | 6.7% | 2.2% | 0.6% | 3.6% | 1.2% |
| MDL | 0.21 | – | | – | |

The FS3700 system configuration consists of a 3180 autosampler, 24 channel peristaltic pump, analytical cartridge consisting of several mixing tees and a single air segmentation tee, a photometric detector equipped with 10 mm flowcell. Samples and calibration curve were prepped with a low nutrient seawater solution. A 640 nm wavelength filter was installed on the photometric for NH3 analysis.

### Principle of Operation – Method

This method is used for the determination of ammonia in estuarine and coastal waters (seawater) according to USEPA Method 349.0 (Reference 3). The ammonia ion reacts with alkaline phenol and dichloroisocyanuric acid (DIC) to form indophenol blue in an amount that is proportional to the ammonia concentration. The blue color is intensified with sodium nitroferricyanide, and the absorbance is measured at 640 nm. The Method Detection Limit (MDL) of this method is 1.0-µg/L nitrogen (0.07 µmol/L nitrogen). The applicable range of the method is 2.0-2,000 µg/L nitrogen (0.15–143 umol/L nitrogen). The range may be extended to analyze higher concentrations by sample dilution.

**Flow Schematic: General flow diagram of the NH3 SFA configuration.**




**Method Parameters**

| | | |
|---|---|---|
| Analysis Settings | Mode | SFA |
| | Load Time | 30 seconds |
| | Cycle Duration | 150 seconds |
| Heater Settings | Enable | 50C |
| UV Lamp Settings | Not Used | |
| Detector Settings | Mode | Photometric |
| | Polarity | Normal |

**Signals/Peak Marking**

| | | |
|---|---|---|
| Peak Measurement | Measure Peaks by | Height |
| | Baseline Value for Peak-marking | Sync-Peak Start as Baseline (default) |
| | Apply Carryover Correction to all Samples | No |
| | Minimum Peak Height | 250 |
| | Minimum Peak Width | 40 |
| Smoothing | Moving Average | 11 points |
| Sync Peak Marking | Recognize Peak Start by a rise of | 500 Counts |
| | ... total counts within | 5 seconds |
| | Sync Peak Ignore Time | 250 seconds |
| | Use Return to Baseline | ✓ |
| | Return-to-Baseline % | 99% |
| | Use D1V | ✓ |

These are suggested initial settings. Adjust as necessary for optimal performance.

**Calibration Table**

| Enable | | Target Concentration |
|---|---|---|
| | STD1 | 0 |
| ✓ | STD2 | 2 |
| ✓ | STD3 | 5 |
| ✓ | STD4 | 20 |
| ✓ | STD5 | 50 |
| ✓ | STD6 | 200 |
| ✓ | STD7 | 500 |
| ✓ | STD8 | 2000 |
| Calibration Curve Fitting Method | | Weighted LInear |
| Calibrant Units | | µg/L |

**MDL, Precision, and Accuracy Study - $NH_3$**

| Parameter $NH_3$ in Seawater | Calibrant 2.0 µg/L | Calibrant 5.0 µg/L | Calibrant 50.0 µg/L | Calibrant 500.0 µg/L | ERA QC Standard 9.03 mg/L |
|---|---|---|---|---|---|
| Replicate 1 | 1.97 | 5.65 | 51.21 | 515.044 | 8.71 |
| Replicate 2 | 2.05 | 5.64 | 51.70 | 518.716 | 8.79 |
| Replicate 3 | 1.91 | 5.64 | 51.75 | 521.547 | 8.96 |
| Replicate 4 | 1.81 | 5.50 | 51.99 | 519.307 | 8.92 |
| Replicate 5 | 1.81 | 5.48 | 51.78 | 519.208 | 8.92 |
| Replicate 6 | 1.80 | 5.46 | 51.47 | 518.302 | 8.78 |
| Replicate 7 | 1.84 | 5.55 | 51.81 | 518.767 | 9.28 |
| Replicate 8 | 1.882 | 5.53 | 51.56 | 520.489 | 8.97 |
| Replicate 9 | – | | 51.83 | 516.607 | 9.10 |
| Replicate 10 | – | | 51.85 | 517.106 | 9.09 |
| Average | 1.88 | 5.56 | 51.70 | 518.509 | 8.95 |
| Standard Deviation | 0.10 | 0.07 | 0.23 | 1.886271 | 0.17 |
| % RSD | 5.1% | 1.3% | 0.4% | 0.4% | 1.9% |
| MDL | 0.29 | – | | – | |

## Section 3. Conclusions

Seawater analysis differs from freshwater analysis. Some chemical reactions can be affected by the salinity of marine waters (the so-called salt effect). Typical seawater contains high amounts of calcium and magnesium, whose salts are insoluble at high pH. This represents a more complex matrix than freshwater or wastewater.

The nutrients that form the basis of life in the ocean are present at concentrations, reportedly 100 million times lower than the typical salt content. This represents a significant challenge to analysts. Measuring low levels of dissolved nutrients require careful attention to detail in cleanliness, sample handling, laboratory technique, and instrument design. The FS3700 provides the best instrument design for reliable and accurate monitoring of seawater nutrients

## Section 4. References

1. Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Cadmium Reduction). Methods for the Chemical Analysis of Water and Wastes; EPA/600/R-79-020; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1984.
2. Nydahl, F. Talanta 1976, 23, 349-357.
3. Nitrogen, Ammonia. Methods for Chemical Analysis of Water and Wastewater; EPA-600/4-79-020; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1997; Method 349.0.

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