

SIO/STS/ODF NUTRIENT DATA BASICS

All data is reported in micro-moles/Liter. NO₃, PO₄, NO₂, and NH₄ are reported to two decimal places and SIL to one.

Normal operating ranges are (in micro moles/liter):

$$\text{NO}_3 + \text{NO}_2 = 0.02 - 46.5$$

$$\text{PO}_4 = 0.02 - 3.60$$

$$\text{Sil} = 0.2 - 180$$

$$\text{NO}_2 = 0.02 - 1.50$$

$$\text{NH}_4 = 0.1 - 6.00$$

The detection limits for the methods/instrumentation are (in micro moles/liter):

$$\text{NO}_3 + \text{NO}_2 = 0.02$$

$$\text{PO}_4 = 0.02$$

$$\text{Sil} = 0.2$$

$$\text{NO}_2 = 0.02$$

$$\text{NH}_4 = 0.1$$

Accuracy is based on the quality of the standards the levels are:

$$\text{NO}_3 = 0.05$$

$$\text{PO}_4 = 0.004$$

$$\text{SIL} = 2-4$$

$$\text{NO}_2 = 0.05$$

$$\text{NH}_4 = 0.03$$

Precision numbers for the instrument are the same for NO₃, PO₄, and NH₄ and a little better for SIL and NO₂ (1 and 0.01, respectively).

NUTRIENT REAGENT PROTOCOL

NITRATE/NITRITE ANALYSIS

A modification of the Armstrong et al. (1967) procedure is used for the analysis of nitrate and nitrite. For nitrate analysis, a seawater sample is passed through a cadmium column where the nitrate is reduced to nitrite. This nitrite is then diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine to form a red dye. The sample is then passed through a 10mm flowcell and absorbance measured at 540nm. The procedure is the same for the nitrite analysis but without the cadmium column.

REAGENTS

Sulfanilamide

Dissolve 10g sulfanilamide in 1.2N HCl and bring to 1 liter volume. Add 2 drops of 40% surfynol 465/485 surfactant.

Store at room temperature in a dark poly bottle.

Note: 40% Surfynol 465/485 is 20% 465 plus 20% 485 in DIW.

N-(1-Naphthyl)-ethylenediamine dihydrochloride (N-1-N)

Dissolve 1g N-1-N in DIW, bring to 1 liter volume. Add 2 drops 40% surfynol 465/485 surfactant.

Store at room temperature in a dark poly bottle. Discard if the solution turns dark reddish brown.

Imidazole Buffer

Dissolve 13.6g imidazole in ~3.8 liters DIW. Stir for at least 30 minutes to completely dissolve. Add 60 ml of CuSO₄ + NH₄Cl mix (see below). Add 4 drops 40% Surfynol 465/485 surfactant.

Let sit overnight before proceeding.

Using a calibrated pH meter, adjust to pH of 7.83-7.85 with 10% (1.2N) HCl (about 20-30 ml of acid, depending on exact strength). Bring final solution to 4L with DIW.

Store at room temperature.

NH₄Cl + CuSO₄ mix:

Dissolve 2g cupric sulfate in DIW, bring to 100 ml volume (2%)

Dissolve 250g ammonium chloride in DIW, bring to 1 liter volume.

Add 5ml of 2% CuSO₄ solution to this NH₄Cl stock. This should last many months.

Nitrate Standard:

In a 1 liter calibrated volumetric "A" flask, dissolve ~1.5xxgm of high purity dried KNO₃ in DIW to make a 1 liter final volume solution. Record temperature of the final solution. Calculate the concentration of this primary nitrate standard using the volumetric flask volume, temperature, and exact weight of standard.

Dilute a secondary and working standards as necessary.

Nitrite Standard:

In a 1 liter calibrated volumetric "A" flask, dissolve ~0.34xxgm of high purity dried NaNO₂ in DIW to make a 1 liter final volume solution. Record temperature of the final solution. Calculate concentration of this primary standard solution using the volumetric flask volume, temperature, and exact weight of standard.

Dilute secondary standard as necessary. Prepare secondary daily.

PHOSPHATE ANALYSIS

Ortho-Phosphate is analyzed using a modification of the Bernhardt and Wilhelms (1967) method. Acidified ammonium molybdate is added to a seawater sample to produce phosphomolybdic acid, which is then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The sample is passed through a 10mm flowcell and absorbance measured at 820nm.

REAGENTS

Ammonium Molybdate

H₂SO₄ sol'n:

Pour 420 ml of DIW into a 2 liter Ehrlenmeyer flask or beaker, place this flask or beaker into an ice bath. SLOWLY add 330 ml of conc H₂SO₄.

This solution gets VERY HOT!! Cool in the ice bath. Make up as much as necessary in the above proportions.

Dissolve 27g ammonium molybdate in 250ml of DIW. Bring to 1 liter volume with the cooled sulfuric acid sol'n. Add 3 drops of 15% DDS surfactant. Store in a dark poly bottle.

Dihydrazine Sulfate

Dissolve 6.4g dihydrazine sulfate in DIW, bring to 1 liter volume and refrigerate.

Note: Hydrazine sulfate may also be used. Dilute 10.0g to 1 liter with DIW.

Phosphate Standard:

In a 1 liter calibrated volumetric "A" flask, dissolve ~0.81xxgm of dried high purity KH₂PO₄ in DIW. Record the temperature. Dilute to the mark with DIW. Calculate concentration using the volumetric flask volume, temperature, and exact weight of standard.

Dilute a secondary and working standards as necessary.

SILICATE ANALYSIS

Silicate is analyzed using the basic method of Armstrong et al. (1967). Acidified ammonium molybdate is added to a seawater sample to produce silicomolybdic acid which is then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. The sample is passed through a 10mm flowcell and measured at 660nm.

REAGENTS

Tartaric Acid

Dissolve 200g tartaric acid in DIW and bring to 1 liter volume. Store at room temperature in a poly bottle.

Ammonium Molybdate

Dissolve 10.8g Ammonium Molybdate Tetrahydrate in 1000ml dilute H₂SO₄*.

*(Dilute H₂SO₄ = 2.8ml conc H₂SO₄ or 6.4ml of H₂SO₄ diluted for PO₄ moly per liter DIW)
(dissolve powder, then add H₂SO₄)

Add 3-5 drops 15% SDS surfactant per liter of solution.

Stannous Chloride

stock: (as needed)

Dissolve 40g of stannous chloride in 100 ml 5N HCl. Refrigerate in a poly bottle.

NOTE:

Minimize oxygen introduction by swirling rather than shaking the solution. Discard if a white solution (oxychloride) forms.

working: (every 24 hours)

Bring 5 ml of stannous chloride stock to 200 ml final volume with 1.2N HCl. Make up daily - refrigerate when not in use in a dark poly bottle.

Silicate Standard:

In a plastic flask, dissolve 0.5642g dried high purity Na₂SiF₆ in about 300ml DIW. This solution will take 4-6 hrs to dissolve. Using this 300ml solution, make up a mixed secondary standard (NO₃, PO₄, SIL) according to oceanic nutrient ranges.

At 1 liter, the silicate concentration is 3000uM.

At 2 liter, the silicate concentration is 1500uM.

AMMONIUM ANALYSIS

Ammonia is analyzed using the method described by Kerouel and Aminot (1997). The sample is combined with a working reagent made up of ortho-phthalaldehyde, sodium sulfite, and borate buffer and heated to 75°C. Fluorescence proportional to the NH₄ concentration is emitted at 460nm following excitation at 370nm.

REAGENTS

Ortho-phthalaldehyde stock (OPA):

Dissolve 8g of ortho-phthalaldehyde in 200ml ethanol and mix thoroughly. Store in a dark glass bottle and keep refrigerated.

Sodium sulfite stock:

Dissolve 0.8g sodium sulfite in DIW and dilute up to 100ml. Store in a glass bottle, replace weekly.

Borate buffer

Dissolve 60g disodium tetraborate in DIW and bring up to 2L volume.

Working reagent:

In the following order and proportions combine:

1L borate buffer

20ml stock orthophthalaldehyde,

2 ml stock sodium sulfite,

4 drops 40% Surfynol 465/485 surfactant and mix.

Store in a glass bottle and protect from light. Replace weekly.

Make this up at least one day prior to use. Store in dark bottle and protect from outside air / NH_4 contamination.

Ammonium Standard:

In a 1 liter calibrated volumetric "A" flask, dissolve ~0.26xxgm of dried high purity $(\text{NH}_4)_2\text{SO}_4$ (ammonium sulfate) in DIW. Record the temperature. Dilute to the mark with DIW. Calculate concentration using the volumetric flask volume, temperature, and exact weight of standard. Dilute a secondary and working standards as necessary.

Armstrong, F.A.J., Stearns, C.A., and Strickland, J.D.H., "The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment," *Deep-Sea Research*, 14, pp.381-389 (1967).

Bernhardt, H., and Wilhelms, A., "The continuous determination of low level iron, soluble phosphate and total phosphate with the AutoAnalyzer," *Technicon Symposia*, I, pp.385-389 (1967).

Kerouel, R., and Aminot, A., "Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis." *Marine Chemistry*, vol 57, no. 3-4, pp. 265-275 (1997).