### Nutrients

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#### Sampling

Seawater samples for nutrient determination were collected at every station and depth into new 15 mL polystyrene tubes after the tube and cap had been rinsed three times with the sample water. A total of 183 unique samples were collected in duplicates. Samples were frozen at -20 °C for later analysis onshore.

##### Standards, reference material samples and reagents

Primary stock standards of nitrate (nitrate + nitrite, NO3, phosphate (PO4) and silicate (SiO4) were prepared at IOS in November 2017 and April 2018; and they were calibrated against Kanso certified reference materials, lot CA (NO3 = 20.21 µM, SiO4 = 37.49 µM, PO4 = 1.442 µM). The primary stock standards were prepared in ultrapure Type I water (Milli-Q water), using high purity grade dry chemicals (Alfa Aesar 99+% for sodium hexafluorosilicate, Fluka TraceSelect grade for potassium nitrate and potassium phosphate monobasic), and grade “A” volumetric flasks, according to Barwell-Clarke and Whitney (1996).

A set of 5 working standards, were prepared daily from the primary standard solutions, using freshly prepared 3.4% sodium chloride/0.02% sodium bicarbonate solution. Concentrations of the standards were selected to bracket the expected nutrient levels in the samples (NO3: 0.00 to 23.97 µM, SiO4 : 0.00 to 71.68 µM and PO4: 0.000 to 2.395 µM.

For quality assurance and quality control purposes, Kanso certified reference material (CRM), deep water reference (DWR), medium check (2nd lowest working standard) and drift cup (D) samples were analyzed at the beginning, middle and at the end of a day’s run. Deepwater sample (depth > 3000m) was collected during the Arctic Joint Ocean Ice Study program cruise in September 2017, sub-sampled into 15 mL polystyrene tubes and frozen at -20°C until day of analysis.

Reagents were prepared as required, using ACS grade dry chemicals, and water from ultrapure water Direct-Q5 system that produced 18.2 mΩ-cm resistance Type I grade water. The system was supplied with the buildings water, pre-treated with 5 µM carbon and 1 µM sediment pre-filters.

##### Sample analysis

Samples were analyzed 1-3 months after collection by Sarah-Ann Quesnel (DFO-IOS) using the Water Properties group’ Seal Analytical nutrient Auto-Analyzer 3 (AA3), following the methods described by the manufacturer, with the exception of omitting the wetting agent in the ammonium chloride reagent for the nitrate + nitrite chemistry and optimizing the flow rate of sample and reagents for the silicate chemistry. Samples were thawed 2 hours prior to analysis in a 25-30°C water-bath and vigorously vortexed for 20 seconds.

A 34 g/L solution of sodium chloride, 0.2 g/L sodium bicarbonate (Sigma, BioXtra grade) was prepared, as needed, and was used to wash the system between samples, to prepare the working standards and as the blank samples. The platen tubing was changed when required (28 August 2018). The cadmium column for nitrate analysis was once on 25 October 2018 as the probe picked up air in a sample that had a leak.

At the beginning of each day, the AA3 was allowed to equilibrate for at least 30 minutes, with reagents and wash solutions hooked-up to the platen tubing. Nitrate, phosphate and silicate were analyzed simultaneously with the AA3. A typical sample run would consist of a drift cup, carryover cup, 5 point standard curve, a set of reference material, a set of cadmium column recovery samples, blanks, followed by a set of stations’ samples. A subset of reference material samples (medium check, Kanso, DWR, drift cup and a blank) was analyzed in the middle of the run and a full set of reference material were analyzed at the end of a day’s run, along with a second set of cadmium column recovery samples. After each run, wash solutions were run through the system for a 20 min cleaning cycle. Data were logged digitally using the AACE software (v.7.07), which calculated all standards, reference materials and sample concentrations, correcting for drift, carryover and baseline. When the nitrate level in surface samples was the same or slightly lower than the sodium chloride solution it was reported as zero.

#### Precision, Accuracy and L.o.D.

The precision was calculated as the pooled standard deviation (*sp*), with outliers rejected by the Chauvenet statistic, and the values for the different sets of samples are given in Table 2 below. Before applying the Chauvenet criteria, some outliers were removed by eye if the difference in nitrate, silicate and phosphate concentrations were greater than ±0.5 µM, ±1 µM and ±0.4 µM respectively.

Table 2. Water Sample Precision, L.o.D. and accuracy summary.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Chemistry Sample** | **Units** | **Minimum Range** | **Maximum Range** | **L.o.D** | **Precision (*s*p)** | **Number of Replicates (*n*)** | **Outliers removed** | **Accuracy (% recovery)** |
| Nitrate (Arctic) | mmol/m3 | 0.00 | 41.32 | 0.02 | 0.08 | 163 | 5 | 96.9-98.4 |
| Silicate (Arctic) | mmol/m3 | 0.23 | 84.71 | 0.12 | 0.18 | 162 | 0 | 97.6-98.9 |
| Phosphate  (Arctic) | mmol/m3 | 0.221 | 2.970 | 0.006 | 0.049 | 162 | 6 | 98.6-100.1 |

The accuracy of nutrient analysis was assured by daily analysis of Kanso CRM for Nutrients in Seawater (RMNS) (batch CA, NO3: 20.21 μmol/L, SiO4: 37.49 μmol/L; PO4: 1.442 µmol/L, salinity: 34.376 PSU). Corrections were applied to the samples when the daily % recovery of the analyte of the Kanso CRM was beyond ± 2% of expected value. The corrected sample value was calculated as follows:

[sample]corr = [sample]uncorr X [Kanso CRM]exp

[Kanso CRM]daily avge

Where, [sample]corr = corrected sample nutrient concentration

[sample]uncorr = measured, uncorrected sample nutrient concentration

[Kanso CRM]exp = expected Kanso certified material nutrient concentration

[Kanso CRM]daily avge = daily average measured Kanso certified material nutrient concentration.

The % recovery of the Kanso RMNS analytes ranged from 96.9-98.4% (n = 23) for NO3, 97.6-98.9% for SiO4 (n = 23) and 98.6-100.1% for PO4 (n = 23). The limit of detection (the mean of 10 blank samples + 3 times its standard deviation) were 0.02 μmol/L for NO3, 0.12 μmol/L for SiO4 and 0.006 μmol/L for PO4.

#### Problems and Solutions

##### Analysis Issues

The Water Properties group’ AA3 was utilized as the Arctic group’s one was in the field until January 2019. After a few test run in early August, I realized that the phosphate tubing was set-up wrong, with wrong point of entry and wrong diameter for most reagents. After rectifying the problem, samples were thawed for analysis. However, more problems occurred and samples were re-frozen until all issues were resolved. Consequently, the first replicate of all samples were thawed twice before the reliable analysis. This didn’t seem to affect the precision as in most cases the data agreed well with that of the second replicates.

#### References