### Nutrients

*Sarah-Ann Quesnel (DFO-IOS)*

*P.I.: Svein Vagle (DFO-IOS)*

#### 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 434 unique samples were collected, of which 426 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 December 2017, and 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, and Fluka TraceSelect grade for potassium nitrate and otassium phosphate monobasic), and grade “A” volumetric flasks, according to Barwell-Clarke and Whitney (1996).

A set of 4 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: 6.05 to 24.18 µM, SiO4 : 12.16 to 48.51 µM and PO4: 0.605 to 2.417 µM for the Arctic samples and NO3: 10.03 to 50.14 µM, SiO4 : 40.28 to 181.22 µM and PO4: 1.004 to 4.014 µM for the North Pacific samples).

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 was collected during the Arctic Joint Ocean Ice Study program cruise in September 2017, sub-sampled into 15 mL polystyrene tubes annd 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 18.0-18.2 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 analysed 5-6 months after collection by Sarah-Ann Quesnel (DFO-IOS) using a Seal Analytical nutrient Auto-Analyser 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 for 2 hours in a 25°C water-bath and vigorously vortexed and shaken for 20 seconds on the day of analysis

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 approximately after 125 hours of operation (26 January 2018). The cadmium column for nitrate analysis was once on 16 January 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 analysed 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 cleaning the system for roughly 20 minutes. Data were logged digitally using the AACE software provided with the AA3 system, 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.

Table . 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 | 18.06 | 0.02 | 0.04 | 228 | 9 | 97.1-98.5 |
| Silicate (Arctic) | mmol/m3 | 0.32 | 54.67 | 0.09 | 0.08 | 218 | 13 | 96.2-98.9 |
| Phosphate (Arctic) | mmol/m3 | 0.135 | 2.420 | 0.008 | 0.059 | 235 | 1 | 98.7-102.4 |
| Nitrate (N.Pacific) | mmol/m3 | 0.00 | 45.82 | 0.03 | 0.05 | 171 | 11 | 97.8-98.5 |
| Silicate\* (N.Pacific) | mmol/m3 | 0.76 | 48.87 | 0.26 | 0.18 | 81 | 6 | 97.1-98.8 |
| Phosphate (N.Pacific) | mmol/m3 | 0.112 | 3.263 | 0.014 | 0.084 | 163 | 13 | 97.4-101.5 |

\* Samples with silicate concentrations greater than 50µM not included as not all the silicate was fully re-dissolved with one thawing cycle and only one set of replicates went through 2 thawing cycles.

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 97.1-98.5% (n = 58) for NO3, 96.2-98.9% for SiO4 (n = 58) and 98.7-102.4% for PO4 (n = 58) for the Arctic samples and 97.8-98.5% (n = 31) for NO3, 97.1-98.8% for SiO4 (n = 31) and 97.4-101.5% for PO4 (n = 31) for the North Pacific samples. The limit of detection (the mean of 10 blank samples + 3 times its standard deviation of 10 blanks) were 0.02 μmol/L for NO3, 0.09 μmol/L for SiO4 and 0.008 μmol/L for PO4 for the Arctic samples and 0.03 μmol/L for NO3, 0.26 μmol/L for SiO4 and 0.014 μmol/L for PO4 for the North Pacific samples.

#### Problems and Solutions

##### Analysis Issues

Silicate Analysis: The Kanso CRM samples occasionnaly came in significantly lower (difference > ±2% of expected value) than the expected value of 37.49 µM, and thus a correction was applied on silicate data on those days, as follows:

 Corrected sample = measured sample X (expected Kanso

 average measured Kanso

Silicate bubble pattern after the 2nd air injection was often irregular and caused the signal (baseline and peaks) to be jagged. When it occurred, samples were re-frozen until problem was addressed. We changed transient tubing, pump tubing, re-made some reagents, etc. Once the problem seemed fixed, the samples were re-thawed and re-analysed. This is when we noticed that silicate in samples with concentrations greater than 50 µM were not completely re-dissolved with one thawing cycle of 2 hours at 25°C. For those samples, only the silicate measured in the re-thawed sample were reported.

#### References