2020-001

CCGS *John P Tully*

Dimethylsulfide (DMS) & Dimethylsulfoniopropionate (DMSP) Report

February 7 – February 25, 2020

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1. Sample Collection

Samples were collected from stations P2, P4 and P12 for DMS. Samples were collected from P2, P4, P12, P16, P20 and P26 for $DMSP_{D\ (dissolved)}$ & $DMSP_{T\ (total)}$.

1.1 DMS

Fourteen water samples from various depths (300m, 200m, 150m, 100m, 75m, 50m, 40m, 30m, 25m, 20m, 15m, 10m, 5m, surface) were collected at station P4 and P12. At P2 there were eleven samples collected (100m, 75m, 50m, 40m, 30m, 25m, 20m, 15m, 10m, 5m, surface). Duplicates were taken at 20m. In all cases, samples were collected in 250 ml ground glass stoppered bottles and stored in a fridge, in the dark and removed one at a time before analysis.

1.2 DMSP

Six samples for both $DMSP_D$ and $DMSP_T$ were collected (200m, 150m, 30m, 20m, 5m, surface). The only exception to this was P2 where there were no 150m or 200m samples, hence, only 4 samples were collected. Duplicates were taken at 20m.

2. Analysis

2.1 DMS

A sample was loaded onto the stripper and purged with UHP Nitrogen for 10 minutes at ~100 ml/min. The DMS was extracted from the water and absorbed onto a Tenax TA trap kept at -80ºC. The trap was subsequently desorbed at 100ºC (with a Dewar containing boiling water) onto a Chromasil 330 column which eluted onto a Flame Photometric Detector (FPD). All samples were run as soon as possible after being collected.

2.2 $DMSP_D$

Approximately 50-75 ml of seawater were allowed to flow directly from the Niskin into a filtration funnel containing a 0.7µm GF/F filter. The first 3.5 ml were collected in a 15 ml or 5 ml polypropylene tube. The entire 3.5 ml was then transferred into a 5 ml, glass, serum bottle and 50 µl of a 50% sulphuric acid/water solution was added. The sample was then crimp sealed and stored in the dark and at 4˚C where it would be analysed back at IOS at a later date.

2.3 $DMSP_T$

Exactly 3.5 ml of seawater were collected directly from the Niskin into a 15 ml or 5 ml polypropylene tube. The entire 3.5 ml was then transferred into a 5 ml, glass, serum bottle and 50 µl of a 50% sulphuric acid/water solution was added. The sample was then crimp sealed and stored in the dark and at 4˚C where it would be analysed back at IOS at a later date.

3. Calibration

3.1 DMS

A four to six level calibration table was used for calculating the concentrations of DMS. The standards were prepared in water and run under the same conditions, as described above, for the samples. A calibration curve was valid for 12 hours. If analysis exceeded 12 hours, a continuing calibration standard was run to ensure the calibration curve was still within acceptable limits.

4. Quality Control

4.1 DMS

System blanks and duplicates were run approximately every 13 samples to ensure the system remained free of contamination and had acceptable reproducibility. Stripping efficiency was evaluated at the beginning of the cruise and was proven to be acceptable at over 97%.

4.2 DMSP

Blanks and duplicates were collected at every station. Blanks were done by simply treating MQ water as an actual sample. For example, in the case of $DMSP_{D,}$ 3.5 mL were collected from a separate funnel and for $DMSP_T$ 3.5 ml were added directly to the polypropylene tube. Like the samples, they were then transferred into a 5 ml, glass, serum bottle and 50 µl of a 50% sulphuric acid/water solution was added. The blank was then crimp sealed and stored in the dark and at 4˚C where it would be analysed back at IOS at a later date.

5. Data & Results

5.1 DMS

The dimethylsulfide system did not perform well on this cruise. Despite being tested out before the cruise, upon reaching Station P2, the system started to behave erratically. Reproducibility and an unacceptable calibration curve resulted in the data for P2 being discarded and P4 samples being collected, but not run for DMS. In an attempt to isolate which component (purge and trap, gas chromatograph or detector) could be causing the problem several parts of the purge and trap were replaced. A calibration was subsequently run and shown to give a very good curve and reproducibility. Another calibration was run before the P12 samples and despite there being some reproducibility issues with standards at the beginning, an acceptable calibration was eventually obtained and the samples were able to be run. The next day all the problems returned. Reproducibility and sensitivity issues plagued the system and the focus turned towards the gas chromatograph and/or detector. The photomultiplier tube in the detector was replaced but it did not have any impact. The detector

was taken apart and cleaned but there was nothing obvious that could be the cause of the problems. The technical notes for the gas chromatograph refer to "sensitivity" issues possibly being caused by a faulty "signal board" in the gas chromatograph and to "replace the board." Unfortunately, the gas chromatograph was over 25 years old and parts such as signal boards are no longer made. In any respect, in an attempt to access the board for inspection, and while putting the detector back together, one of the wires for the ceramic heater disintegrated upon touch due to decades of heating and cooling. As with the signal board, the manufacturer no longer makes heaters for this model of GC and for all intents and purpose the system, at that point, became inoperable. No DMS samples were collected for P16, P20 or P26.

5.2 DMSP

The DMSP samples were collected for all stations. These samples were run in April 2020 back in the laboratory. The data were good and there was no problems with contamination due to storage that has plagued the analyses in the past.

6. Conclusions

6.1 DMS

The problems encountered with the DMS system were, unfortunately, a product of not replacing old equipment and keeping up to date with technology and innovation. This was a problem that was identified a couple of years ago and, at that time, a plan was implemented to upgrade the DMS instrumentation. In 2019 a new GC was ordered and preliminary plans were made to begin the upgrading process to prevent exactly what happened on this cruise. Ironically, the GC was delivered in January 2020, but not in time to put into service for the February cruise. It is planned to have the new system operational by February 2021. In the interim, an attempt will be made to configure an older GC and have it operational by summer.

6.2 DMSP

We have now officially moved away from storing DMSP samples in plastic tubes and now store them in glass serum bottles. Additional storage studies will be required to determine the maximum storage time but, without question, moving to glass bottles for storage, versus plastic tubes, and analysing the samples within a couple of months, has alleviated the contamination problems seen in the past.