Hein J.W. de Baar & Rob Middag (2009)

Sampling and Analytical Methodology

Samples were taken using 24 internally Teflon-coated PVC 12 litre GO-FLO Samplers (General Oceanics Inc.) mounted on an all-titanium frame. This frame was connected to a 17.7 mm diameter Kevlar hydrowire with seven independent internal signal/conductor cables (Cousin Trestec S.A.) and controlled from onboard. Each GO-FLO sampler had a special ultraclean all-teflon PTFE valve (Cole Parmer; PN A-06392-31) installed. Samples for trace metal analysis were collected from the GO-FLO bottles in a class 100 clean room environment. The water was filtered over a 0.2 μm filter cartridge (Sartrobran-300, Sartorius) under pressure (1.5 atm) of (in-line prefiltered) nitrogen gas exerted via a special connector instead of the regular air bleeding valve at the top of each GO-FLO sampler. Sub-samples for Al were taken in cleaned LDPE sample bottles (125 mL) from each GO-FLO bottle. All sample bottles were rinsed five times with the sample seawater.

Analyses of dissolved Al were based on a method developed by Resing and Measures (1994). Samples were stored in a refrigerator (4 °C) and analysed usually within 24 h after sampling but always within 36 h. Samples were acidified at least 1 h before analyses with 12 M ultraclean HCl (Baseline® Hydrochloric Acid, Seastar Chemicals Inc.) to a pH of 1.8. In a flow injection system the samples were buffered inline to a pH of 4.8 ± 0.1 with ultraclean 0.6 M ammonium acetate buffer. This buffer was produced by diluting a saturated solution of ammonium acetate crystals to an 0.6 M solution with MQ. The pH was subsequently adjusted to 6.7 with ultraclean ammonium hydroxide. This was produced by bubbling 0.2 μm filtered high purity ammonia gas through MQ water.

The buffered sample was pre-concentrated for 240 s on a Toyopearl AF-Chelate 650M (TosoHaas, Germany) column. Hereafter the column was rinsed for 60 s with MQ water to remove interfering salts. The Al was subsequently eluted from the column with 0.16 M HCl (Suprapure, Merck) during 250 s. The eluate of Al in HCl entered the reaction stream which consisted of a lumogallion (Pfaltz & Bauer) solution in 4 M ammonium acetate buffer. The 4 M buffer was produced similar to the 0.6 M buffer (see above), but with the pH adjusted to 6.8 ± 0.1 and the lumogallion was a 4.8 mM solution in MQ. The mixing of the HCl and buffer results in a reaction pH of 5.7 ± 0.1 at which an Al-Lumogallion chelate complex is formed which can be detected by its fluorescence. The complex was mixed in a 10 m reaction coil placed in a water bath of 50 °C. Hereafter a 2.5% Brij-35 (Merck) solution in MQ was added to increase the sensitivity (Resing and Measures, 1994) and mixed in a 3 m mixing coil. Afterwards the emission of the fluorescent complex was detected on a FIA-lab PMT-FL detector with a 510 until 580 nm emission filter and a 480 until 490 nm excitation filter. Concentrations of Al were calculated in nanomol.L-1 from the peak heights. The system was calibrated using standard additions from a 5000 nM Al stock solution (Fluka) to filtered acidified seawater of low Al concentration that was collected in the Arctic Ocean. A six-point calibration line (0, 1, 2, 4, 8 and 16 nM standard additions) and blank determination were made every day. The 3 lowest points (0, 1 and 2 nM) of the calibration line were measured in triplicate and the 3 highest points (4, 8 and 16 nM) in duplicate in order to add more weight to the lower part of the calibration line. The blank was determined by plotting the signals of increasing pre-concentration times (30, 60, 120, 210 and 300 seconds) of the water also used for the calibration. A line was fitted through these data points and the intercept of the line taken as the blank, which was usually below 0.2 nM. If the blank was greater than 0.2 nM, the analysis run was stopped. Subsequently the system was cleaned and the blank reanalysed with freshly made sampling buffer until the blank value was below the 0.2 nM limit. The limit of detection, defined as three times the standard deviation of the lowest concentration observed, was 0.15 nM. The FIA system was cleaned every day by rinsing with a 0.5 M HCl solution.

Data Processing

A standard was measured in triplicate every day. This standard was a sub-sample of a 25 L volume of filtered seawater that was taken at the beginning of the cruise in the Barents Sea. The relative standard deviation of the replicate analysis seawater sample that was analysed 27 times on different days in triplicate was 3.19%. The relative standard deviation on single days was on average 2%. The average Al concentration of this standard was 4.93 nM and the deviation from this average for a given measuring day was used as a correction factor. To verify whether this was decreasing the inter-daily variability in the dataset, every day a sample which was collected and measured the previous measuring day, was analysed once again. The deviation between the concentrations measured on the different days decreased from 3.6% to 2.8%, indicating the data correction is beneficial. Moreover, samples of the SAFe intercalibration program (Johnson et al., 2007) were analysed in triplicate (Table 1). It appears that the Al concentration in bottle S #252 is slightly higher than the concentration for surface (S) water found by Brown and Bruland (2008), but not statistically different. Bottle S #425 is in almost perfect agreement, as is bottle D2 #3 for deep (D2) water from 1000m. The dataset was scanned for obvious outliers and these have been quality flagged with the number 4. Some samples gave anomalous nutrient results for the intended depth and were assumed to have been closed at the wrong depth and quality flagged with the number 8. All other values are assumed to be correct and flagged with the number 0

Related files and references

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