CTD bottle data ARK-XXII/2 – The Ultra Clean CTD system (UCC)

PI: Patrick Laan, Sven Ober, Lorendz Boom, Karel Bakker
Royal Netherlands Institute for Sea Research

Along the five sections of this cruise (Schauer, 2008) altogether 191 CTD profiles were taken at 127 stations and water samples were collected. 142 casts were carried out with a standard CTD/rosette water sampler and 49 casts were taken with the ultra-clean system of the GEOTRACES programme. Both systems had Seabird CTD components (SBE 911+) with double temperature and conductivity sensors.

The Ultra Clean CTD system (UCC), Sven Ober, Patrick Laan, Lorendz Boom, Royal Netherlands Institute for Sea Research

During the cruise a special CTD-system was used to sample for trace-elements and isotopes. This CTD-system consists of 3 major modules: a winch with a superaramide CTD-cable, a box-shaped titanium CTD-frame and a clean air container that is designed to hold the CTD-frame in order to enable subsampling and filtration under clean air conditions. The CTD-frame is made of pure titanium and was equipped with a Seabird SBE9+ CTD underwater unit, a SBE3 thermometer, a SBE4 conductivitysensor, a SBE5 underwater pump, a SBE43 DO-sensor, a Chelsea MK-III fluorometer, a Seapoint OBS and a special sampling-system. This sampling-system consists of a Multivalve hydraulic multiplexer and 24 GoFlo sampling bottles each with its own hydraulic release unit. (De Baar et al., 2007; Ober et al., 2002). In addition to the above mentioned sensors a Dr. Haardt fluorometer type BackScat 1 for detecting yellow substance was mounted from station 266, cast 1. From station 371, cast 2 the Aquatracka fluorometer was dismounted and a WetLabs C-Star transmissometer was mounted instead. In total 49 casts were carried out with the UCC-system including 2 test casts.
Throughout the whole cruise the system worked very reliably, although some small technical problems occurred. The conductivity-sensor had to be exchanged for a spare because it appeared to have a slightly shifted calibration (although it was calibrated recently) and the OBS had to be exchanged, because this sensor apparently did not survive the pressure during the deepest cast of the cruise (5,220 m) although this sensor was rated up to 6,000 m. The Dissolved Oxygensensor showed erratic values at depths over about 2,000 m. This problem was solved by exchanging the cable between the sensor and the underwater unit. At steep gradients some salinity-spiking was observed. Possible cause is the changed duct of the CTD. The longer tubes slow down the flow of the water and therefore the standard timing of the sensors is not optimal. This will be become clear during postprocessing of the data in the near future. In case the retuning of timing of the sensors will not solve the spiking the most probable cause is a disturbed flow near the sensors. Another, more free-flow, location for the sensors in the frame must be considered.
The hydraulic bottle control system worked perfectly (100 %) and the GOFLO samplers worked almost perfectly (99 % based on nutrient data). Prior to the cruise the edges of the holes in the top and bottom closing spheres of each Go-FLO sampler were made less sharp and prior to each cast all the spheres were sprayed with Teflon spray. These efforts clearly paid off.

Highest priority was given to the sampling of complete vertical profiles throughout the complete (4 - 5 km depth) water column at deep water stations in the different central Arctic Ocean basins. The sampling depth differed from 33 meter as the shallowest station, in the Laptev Sea, up to 5,220 meter for the deepest station at the south of the Gakkel Ridge. From these 49 casts 27 were deeper than 2,000 meter.

References

De Baar H. J. W., Timmermans K. R., Laan P., De Porto H. H., Ober S., Blom J. J., Bakker M. C., Schilling J., Sarthou G., Smit M. G., and Klunder M. (2008) Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program. *Marine Chemistry* **111**(1-2), 4.

Ober S., Groenewegen R. L., Boekel H. J., Keijzer E. J. H., Derksen J. D. J., and Laan M. (2002) A new way of oceanographic watersampling. Abstract of presentation at Inmartech, 8 October 2002, Yokusuku, Japan. http://www.jamstec.go.jp/jamstece/whatsnew/inmartech2002/programme.pdf.

Schauer U. (2008) The expedition ARKTIS-XXII/2 of the research vessel "Polarstern" in 2007 / ed. by Ursula Schauer with contributions of the participants. *Reports on polar and marine research* **579**, 271 pp.

Nutrient analyses during ARK-XXII/2

PI: Karel Bakker, Royal Netherlands Institute of Sea Research

Equipment and methods

Nutrients during the expedition ARK-XXII/2 (Schauer, 2008) were analysed in a thermostated laboratory container with a Technicon TRAACS 800, continuous flow auto-analyser. The sample rate was set at 60 samples per hour, measuring about 4,500 samples during the cruise. Measurements were made simultaneously on four channels: phosphate, silicate, nitrate and nitrite together, and nitrite separately. All measurements were calibrated with standards diluted in low nutrient seawater LNSW, and LNSW was used as wash water between the samples.

The colorimetric methods used are as follows

- Phosphate: Ortho-phosphate is measured by formation of a blue reduced Molybdophosphate-complex at pH 0.9-1.1. Potassium Antimonyltartrate used as the catalyst and ascorbic acid as a reducing agent. The absorbency is measured at 880 nm. (Murphy, J. & Riley, 1962).
- Silicate: Measured as a blue reduced Silicomolybdenium-complex at 800 nm. Ascorbic acid is used as reducing agent and oxalic acid is used to prevent interference of phosphate. (Strickland and Parsons, 1972).
- Nitrite: Diazotation of nitrite with sulfanylamide and N-(1-naphtyl)-ethylene diammonium dichloride to form a pink dye measured at 550 nm.

- Nitrate and Nitrite (here called Nox): Nitrate is first reduced in a copperized cadmium coil using imidazole as buffer and is then measured as nitrite at 550 nm. (Grasshoff et al., 1983).

Sample handling
The samples were collected in 100 ml high-density polyethylene sample bottles, after first being rinsed three times with a small amount of the sample, taken directly from the CTD-rosette bottles. The samples were kept cool and dark, stored in a refrigerator and analysed normally within 10 hours and within 16 hours as a maximum. Analyses were carried out using high-density polyethylene "pony-vials" with a volume of 6 ml, they were rinsed three times before filling with the samples. For duplicate analysis purposes between runs, the deepest sample at every station was capped in a pony-vial to be measured for a second time during the next run. To avoid evaporation during the runs, all vials including the calibration standards used were sealed with "parafilm" under tension, so that a sharpened sample needle easily penetrated through leaving a small hole in the film.

Calibration and Standards
Nutrient primary stock standards were prepared at the home laboratory, NIOZ.

- Phosphate: by weighing Potassium dihydrogen phosphate in a calibrated volumetric PP flask set to 1mM PO_4.
- Silicate: for silicate a certified standard (Merck) was diluted until 1.78 mM Si (stored at room temperature in an 100 % humidified box).
- Nitrate: weighing in Potassium nitrate set to 10mM NO_3.
- Nitrite: weighing in Sodium nitrite set to 1mM NO_2.

The calibration standards were prepared daily by diluting the separate stock standards, using three electronic pipettes, into four volumetric 100 ml PP flasks (calibrated at the lab) filled with low nutrient sea water LNSW. The blank values of the LNSW were measured on board and added to the calibration values to get the absolute nutrient values.

Cocktail standard
This standard acts as a lab reference and its use is described under "quality control". It is made in the laboratory containing phosphate, silicate and nitrate in a solution containing 40 mg Hg_2Cl_2 per litre as a preservative. Every time it was used it was diluted 250 times with the same pipette, and the same volumetric flask.

Quality Control
Our standards have already been proven by inter calibration exercises like ICES and Quasimeme, and the RMNS exercise organised 2006 from Michio Aoyama MRI/Japan, to be within the best obtainable limits to the mean of the better laboratories. To gain some accuracy the Cocktail standard is monitored now since 1997, showing between run reproducibility better than 1.5 %, but typically 0.7 % of its average value.

	average value	S.D	N
PO_4	086 μM	0.008μM	74
SiO_2	13.5 μM	0.054μM	74
NO_3	13.9 μM	0.091μM	52

The advantage of a cocktail standard is like using a reference standard with three nutrients mixed into one bulk, giving for each run a quite good overview of how the instrument is performing. It also provides a methodology to correct data from run to run for producing better isoline-plots from station to station along horizontal surfaces within the ocean.

In preceding cruises, especially in an area like the Weddell Sea, where nutrient gradients in deep water are very small, back-correction (implying a factor in each run to multiply with, for gaining the average cocktail value after the whole transect in each run) with use of the cocktail is absolutely necessary to be able to discern the small true differences between samples.

Others have reported the use of a real reference standard supplied from deep water (2,000 m) but this turns out to be not stable over a period longer than three weeks. However during the second transect of the current cruise, the cocktail-based data produced was well within expected performance, so back-correcting afterwards is not necessary.

During the cruise, a graph was made for all the runs with a listing of the cocktail values. So bad runs were easily recognised if a value was not within the alarmsettings of +/- 1.5 % (this was typically better than +/- 1 %). Deviations beyond the +/– 1.5 % verification setting, did upon further verification, usually show up as irregularities of the analyser instrument (as noisy peaks, or gain calculation problems etc.), upon which the given samples were then re-analysed.

Statistics

For most of the nutrient parameters in this area it was not interesting to calculate the mean detection limit MDL. The exception was NO_2, which showed a few small detectable peaks at the surface layer, and for the rest of the profile values around or below detection limits smaller then 0.01 µM. In the same statistical run the MDL was calculated as well as the standard deviation on standards at two levels. Mean Detection Limits (calculated as 6 x S.D. of the sampled baseline water)

	μM	Used measuring ranges μM
PO_4	0.01	1.50 *
SiO_2	0.01	18.0 *
NO_3+NO_2	0.03	21.0
NO_2	0.007	1.00

* for SiO_2 the preset range of the instrument was raised in the most Eastern part of the cruise region, to higher range of 31 µM, and similarly for PO_4 to higher range of 2 µM. This was necessary because of the highly nutrient-enriched waters derived from the Pacific Ocean at a depth around 70 - 125 m.

Reproducibility: of 5 sample bottles at two levels given with coefficient of variation %

	level I	Std dev.	Cv %	level II	Std dev.	Cv %
PO_4	0.193 μM	0.002	0.85	0.96 μM	0.002	0.17
SiO_2	2.504 μM	0.001	0.39	8.772μM	0.021	0.24
NO_3+NO_2	0.312 μM	0.004	1.43	13.648μM	0.029	0.22
NO_2 *	0.010 μM	0.001	0.11*	0.41μM	0.002	0.20*

* For NO_2 the % listed is the percentage of the full scale value due to the low natural concentration in the seawater being only lower than 40 % of full range! In order to obtain better values, an attempt was made to scale in the range for the nutrients to be measured such that the maximum was always at a level of 60 - 90 % of full scale.

Cross-runs statistics

In order to obtain cross-run statistical values, analyses were carried out twice on the same sample from the bottle closed at the bottom layer in the first run, and in the consecutive run. This provides the possibility to estimate the precision from station to station in a horizontal way. It is well known that the reproducibility within one calibrated run for an auto analyser is much better than measurements made across several runs, with each run having its own calibration settings. Analysis of these (cross runs) duplicate samples shows that the absolute differences are for

PO_4 to be s.d.0.015µM (avg. level 0.9µM PO_4 n=23)
SiO_2 to be s.d.0.131µM (avg. level 8.17µM SiO_2 n=23)
NO_3+NO_2 to be s.d.0.175µM (avg. level 12.70µM NO_3+NO_2 n=23)

In the raw data set of the first transect, due to the improvement in temperature stability during following transects those values will improve especially for PO_4 to better than 0.01 µM. Nevertheless, for our cocktail standard measured in every run, the resulting values remained stable for all nutrients during the cruise. In the future it would be highly advisable to produce and distribute a certified nutrient reference material, like the standard seawater for salinity, DIC, DOC. Such approach is now being pursued in the international community, and very likely would greatly improve the true accuracy, hence much improved compatibility of data better comparison between various laboratories and cruises.

Problems

Temperature stability of the laboratory container in the first week, using an airconditioning unit just diagonal opposite the analyser, gave a data offset been seen in recording the cocktail standard in a plot of +/ 0.02 µM PO_4. Just by placing a kind of sieve curtain between the air-conditioner and the analyser to lead the cold air not

massively, but gently towards the other half of the container where the analyser is placed, largely solved this problem. This curtain improved the temperature stability within 1° C instead of 2° C, and reduced the cross-run offset in the cocktail for PO_4 to +/- 0.01 µM on a value of 0.86 µM PO_4.

Evaporation during analysis

After the first two transects, I noticed that evaporation of sample water in the sampler-tubes can effect the data depending on the length of the run and the volume in the tube; evaporation was about 1.6 % per day, so 0.1 % within a run from start to end (measured relative humidity in the lab-container was around 23 %!!). It was clear that all sample tubes in the sampler should be covered with parafilm, although there is routinely made a gain-drift control assuming that the drift for all samples tubes is linear.

References

Grasshoff K., Ehrhardt M., and Kremling K. (1983) *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, 419pp.

Murphy J. and Riley J. P. (1962) A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* **27**, 31-36.

Schauer U. (2008) The expedition ARKTIS-XXII/2 of the research vessel "Polarstern" in 2007 / ed. by Ursula Schauer with contributions of the participants. *Reports on polar and marine research* **579**, 271 pp.

Strickland J. D. H. and Parsons T. R. (1972) A Practical Handbook of Seawater Analysis, 2nd edition. *Bull.Fish.Res.Board Canada* **167**, 310pp.