

## **CTD bottle data ARK-XXII/2 – The standard AWI CTD system**

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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 standard CTD system**

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The standard CTD system, SN 485, from Sea-Bird Electronics Inc SBE911+ was equipped with duplicate temperature and conductivity sensors (temperature sensors SBE3, SN 2423 and 2460, conductivity sensors SBE4, SN 2078 and 2054 and pressure sensor Digiquartz 410K-105 SN 68997). The CTD was connected to a SBE32 Carousel Water Sampler, SN 202, with 24 12-liter bottles. Additionally, a Benthos Altimeter PSA-916, SN 1228, a Wetlabs C-Star Transmissometer, SN 946, and a SBE 43 dissolved oxygen sensor, SN 743, was mounted on the carousel. The SBE 43 contains a membrane polarographic oxygen detector. The algorithm to compute oxygen concentration requires also measurements of temperature, salinity and pressure which are provided by the CTD system. To calibrate the oxygen profiles 279 water samples at 30 CTD casts were collected and measured onboard with Winkler titration. Continuous profiles of the DOM concentration were obtained with two fluorometers, a Wetlabs ECO-CDOM, SN 742, and a Dr. Haardt Back Scat Model 1184.6, SN 12030. Salinity of 245 water samples was measured using a Guildline salinometer with Standard Water Batch P148 for calibration of the salinity sensor.

### **Nutrient analyses during ARK-XXII/2**

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#### **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  $\text{PO}_4$ .
- 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  $\text{NO}_3$ .
- Nitrite: weighing in Sodium nitrite set to 1mM  $\text{NO}_2$ .

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  $\text{Hg}_2\text{Cl}_2$  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 <sub>4</sub>	086 $\mu$ M	0.008 $\mu$ M	74
SiO <sub>2</sub>	13.5 $\mu$ M	0.054 $\mu$ M	74
NO <sub>3</sub>	13.9 $\mu$ M	0.091 $\mu$ M	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<sub>2</sub>, 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 than 0.01  $\mu$ M. 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)

	$\mu\text{M}$	Used measuring ranges $\mu\text{M}$
<b>PO<sub>4</sub></b>	<b>0.01</b>	<b>1.50 *</b>
<b>SiO<sub>2</sub></b>	<b>0.01</b>	<b>18.0 *</b>
<b>NO<sub>3</sub>+NO<sub>2</sub></b>	<b>0.03</b>	<b>21.0</b>
<b>NO<sub>2</sub></b>	<b>0.007</b>	<b>1.00</b>

\* for SiO<sub>2</sub> the preset range of the instrument was raised in the most Eastern part of the cruise region, to higher range of 31  $\mu\text{M}$ , and similarly for PO<sub>4</sub> to higher range of 2  $\mu\text{M}$ . 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 %
<b>PO<sub>4</sub></b>	<b>0.193 <math>\mu\text{M}</math></b>	<b>0.002</b>	<b>0.85</b>	<b>0.96 <math>\mu\text{M}</math></b>	<b>0.002</b>	<b>0.17</b>
<b>SiO<sub>2</sub></b>	<b>2.504 <math>\mu\text{M}</math></b>	<b>0.001</b>	<b>0.39</b>	<b>8.772 <math>\mu\text{M}</math></b>	<b>0.021</b>	<b>0.24</b>
<b>NO<sub>3</sub>+NO<sub>2</sub></b>	<b>0.312 <math>\mu\text{M}</math></b>	<b>0.004</b>	<b>1.43</b>	<b>13.648 <math>\mu\text{M}</math></b>	<b>0.029</b>	<b>0.22</b>
<b>NO<sub>2</sub> *</b>	<b>0.010 <math>\mu\text{M}</math></b>	<b>0.001</b>	<b>0.11*</b>	<b>0.41 <math>\mu\text{M}</math></b>	<b>0.002</b>	<b>0.20*</b>

\* For NO<sub>2</sub> 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<sub>4</sub> to be s.d.0.015 $\mu\text{M}$  (avg. level 0.9 $\mu\text{M}$  PO<sub>4</sub> n=23)

SiO<sub>2</sub> to be s.d.0.131 $\mu\text{M}$  (avg. level 8.17 $\mu\text{M}$  SiO<sub>2</sub> n=23)

NO<sub>3</sub>+NO<sub>2</sub> to be s.d.0.175 $\mu\text{M}$  (avg. level 12.70 $\mu\text{M}$  NO<sub>3</sub>+NO<sub>2</sub> 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<sub>4</sub> to better than 0.01  $\mu\text{M}$ . 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  $\pm 0.02 \mu\text{M PO}_4$ . 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  $1^\circ \text{C}$  instead of  $2^\circ \text{C}$ , and reduced the cross-run offset in the cocktail for  $\text{PO}_4$  to  $\pm 0.01 \mu\text{M}$  on a value of  $0.86 \mu\text{M PO}_4$ .

### **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**

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