Cruise report: GEOTRACES Test cruise

Transit Texel-Scrabster (Scotland)

R/V Pelagia cruise 64PE318, 23-27 April 2010

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with contributions from participants

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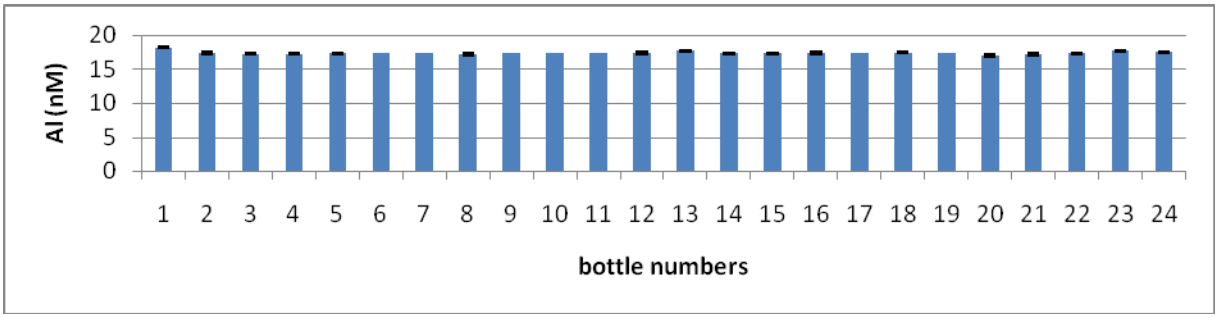
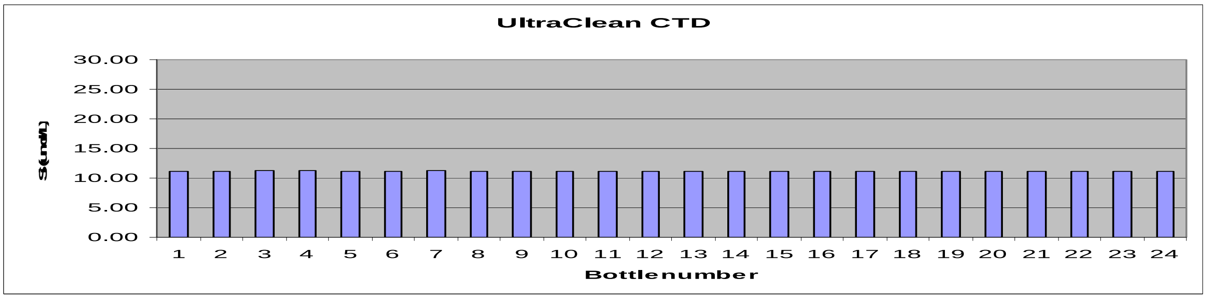
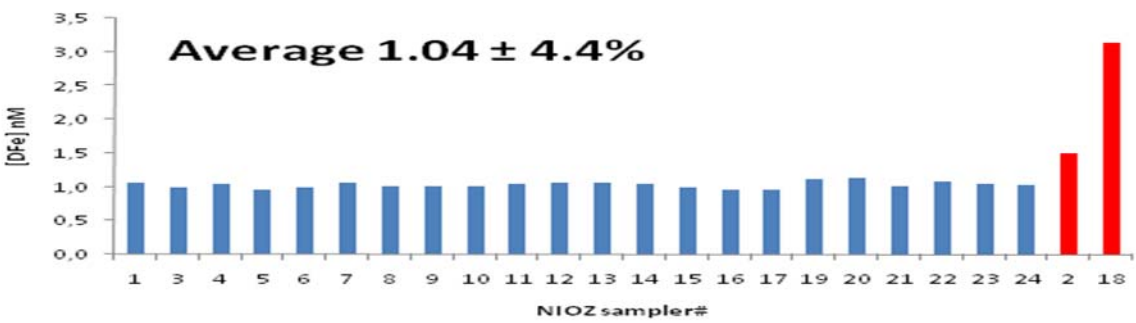






Summary

Apart from being a transit to the starting position of the Geotraces cruise Iceland-Bermuda this cruise was used for testing the two new CTD frames with 24 new large volume bottles deployed with a new Kevlar hydro wire cable. One the ultraclean all-titanium frame, collecting 24 samples of 27 Litres with novel butterfly-valve type ultraclean samplers made from clean PVDF plastic. The other consists of 24 new Niskin-type samplers of large 25 L volume were manufactured and mounted on a new stainless steel frame.

This cruise had still another aim to train five international PhD students in clean sampling, financed by COST Action. Due to the closure of the airports only two students Ana-Marija Blateric and Gregory de Souza could join the cruise. PhD student Marco van Hulten joined the cruise as part of the GEOTRACES team.

The butterfly-type valves in top and bottom of the samplers in the Ultra Clean CTD, worked perfectly from the first cast. A few valves and nipples showed some leakage when pressurised to sample the bottles in the clean container. These problems were improved after minor adjustments. Some parts need to move more flexible. The necessary modifications can only be realised for the second leg of Geotraces.
A final test of the two new CTD systems was performed N-E of Scotland (60° 6' 0.356''N and 5° 47' 38.76''W), where all 48 bottles were closed at the same depth, near the bottom. Nutrient concentrations showed that all the samplers contained indeed water from the same depth proving that the butterfly-valves closed the samplers properly. Al and Fe concentrations measured in the 24 bottles of the ultra clean CTD showed that the new ultra clean NIOZ sampler bottles are suitable for trace metal analyses.

We acknowledge ZKO (project number 839.08.410) for funding of this work.

1. Introduction

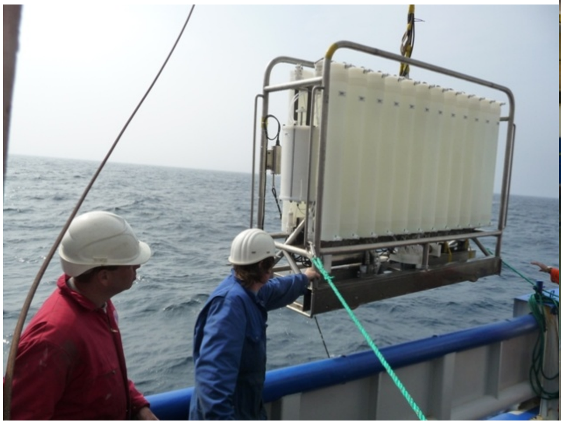
Cruise 64PE318 was a very special cruise since it was the first cruise after the midlife refit of Pelagia. We had the honour to be on board on a new ship with an extremely beautiful dark blue hull colour. An upgraded ABC with Casino+ a voyage logbook that is indeed easy to handle. The communication lines with the outside world have greatly been improved. Having internet proved to be very helpful indeed. The organization in the mess room with the new big table is very agreeable for eating but also for meetings. It was very nice to be on the first cruise, but it had its drawbacks also, little failures, little problems that needed to be solved.

The cruise was originally planned as a transit between Texel and Iceland during which two new CTD systems would be tested, a new ultraclean CTD and a large volume CTD with Niskin type bottles. In Iceland the first of the three Geotraces cruises would start. However the airport at Reykjavik, Iceland was closed due to the ash plume from the volcano under the Eyjafjallajoekull it was decided that the port stop for exchanging scientists and fuelling intended at Reykjavik at 29 April was changed into Scrabster Harbour in northernmost

Scotland at 27 April. Travel to and from the ship by nine and five scientists, respectively was diverted accordingly.

2. Cruise aims

Apart from being a transit to the starting position of the Geotraces cruise Iceland-Bermuda this cruise was used for testing the two new CTD frames with 24 new large volume bottles deployed with a new Kevlar hydro wire cable. One the ultraclean all-titanium frame, collecting 24 samples of 27 L with novel butterfly-valve type ultraclean samplers made from clean PVDF plastic. The other consists of 24 new Niskin-type samplers of large 25 L volume were manufactured and mounted on a new stainless steel frame.




Figures 1 and 2: both frames, left the Ultraclean CTD, right the large volume CTD..

This cruise had still another aim to train five international PhD students in clean sampling, financed by COST Action. Also two guests, colleagues from China and India were invited to join the cruise to see and learn the way NIOZ can do the metal clean sampling. The Geotraces PhD student Marco van Hulten who will do modelling on the Geotraces data would be our eighth guest for learning how the data for his modelling work was obtained.
Also this program was frustrated by the volcanic eruption in Iceland, Because both Schiphol airport and Reykjavik airport Kevlavik were closed. Only three of the six PhD students joined the cruise.

3.Participants

Loes Gerringa (PI)	NIOZ-BIO
Micha Rijkenberg	NIOZ-BIO
Patrick Laan	NIOZ-BIO
Rob Middag	NIOZ-BIO
Lesley Salt	NIOZ-BIO
Jan van Ooijen	NIOZ-CHEM
Martin Laan	NIOZ-MTE
Edwin Keijzer	NIOZ-MTI
Lorendz Boom	NIOZ-MTM
Sven Ober	NIOZ-FYS
Steven van Heuven	University Groningen
Gregory de Souza	Swiss Federal Institute of Technology, Zurich
Ana-Marija Blataric	Ruder Boskovic Institute, Croatia
Macro van Hulten	KNMI
Patrick Schmidt	University of Bremen

4. Results

4.1 Testing of the new CTD-systems (Martin Laan, Edwin Keijzer, Sven Ober)

During the first days of the cruise the assembly of the UC CTD-system was finished. In the titanium frame with 24 newly developed water samplers made of (ultraclean) PVDF and titanium were mounted.
The butterfly-type valves in top and bottom of the samplers, accumulator and modified Multivalve worked perfectly from the first cast. The samplers passed the air/water-interface with closed valves, the valves opened automatically at about 30 meters depth (= GoFlo-functionality) and were fired all just above the bottom one by one. After the cast in the clean container the bottles were pressurised with nitrogen to enable fast filtration during sampling. A few valves and nipples showed some leakage. These problems were improved after minor adjustments. Some parts need to move more flexible. The necessary modifications can only be realised for the second leg of Geotraces. Nutrients- and aluminium -concentrations were determined and showed that all the samplers contained water from the same depth proving that the butterfly-valves closed the samplers properly.

Beside the UC CTD-system a so called Large Volume CTD (CTD 25 L)was tested. In this enlarged CTD-frame 24 25-liter-Niskins (instead of the usual 12-liter-sampler) were mounted. This CTD worked properly too.

Both CTD-systems were equipped with a Seabird SBE-9+ underwater-unit, a SBE 3+ thermometer, a SBE4-conductivity-sensor, a SBE 5T under-water pump, a Chelsea Aquatracka fluorometer and a Wetlabs CStar- transmissiometer. For bottom-detection a bottom-switch was mounted and as "early-warning" system a Benthos PSA-916 altimeter was applied. The altimeters were new sensors and worked surprisingly good. Bottom detection was possible from 60 to 80 meter distance from the bottom and this is of great help for both the CTD- and the Winch-operator. CTD- operations can now be done much safer than in the past.

Both CTD-system were lowered through the water column using the new and very long (about 9500 m) super-aramide-cable and the big Kley-France winch. During the first cast the electric engines of the winch generated too much electrical noise and voltage-peaks. The telemetry between deck unit and CTD-under-water unit was disturbed significantly. The problems were solved by installing an isolation-transformer between mains and the deck unit, applying optical RS-232 couplers between deck unit and logging computer and improved grounding of the winch. These measures together were very effective and the CTD-telemetry was perfect after that.

Figure 3 : Happy faces after the first test of the UC CTD

Figure 4: Emptying the large volume of the 25 L bottles

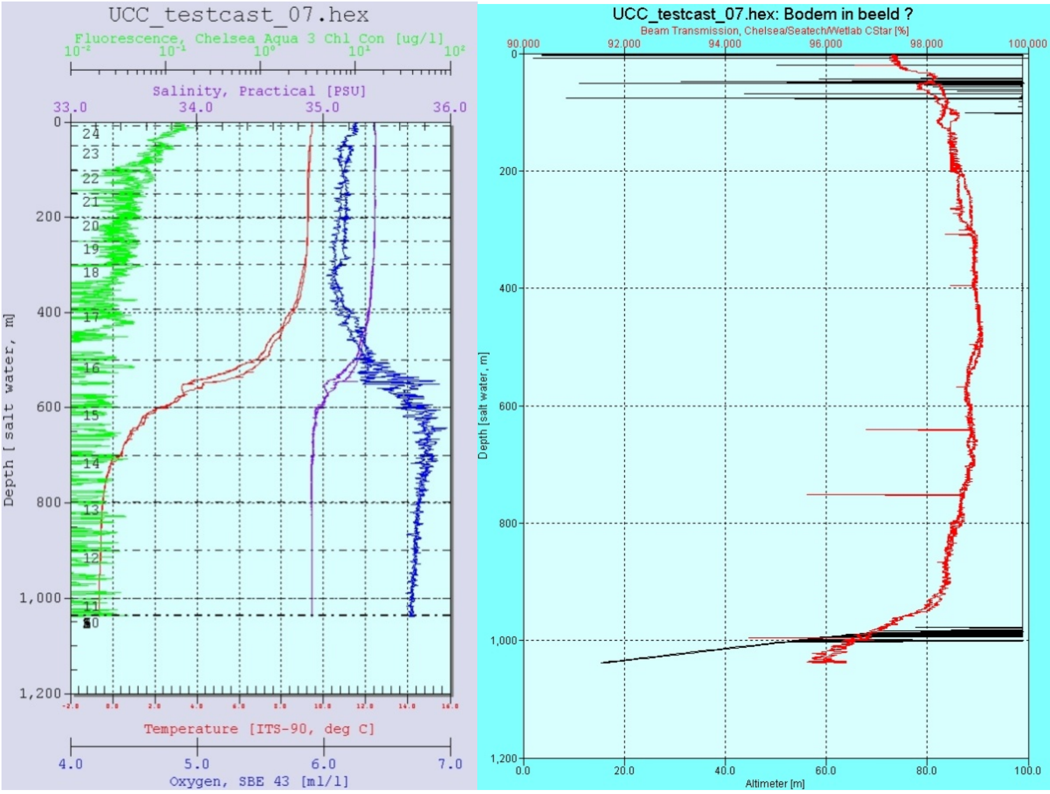


Figure 5: CTD data from teh test station

4.2 Chemical analysis

4.2.1 Nutrients

Jan van Ooijen

Summary:

To see if the bottles of the CTD were all closed at the same depth and that they were not leaking on the way up I sampled all bottles, which were closed near the bottom, and analysed the content of the water on Silicate. This was done for the Ultra Clean CTD as well as for the 25 Litre CTD.

Method:

All samples were taken in a 100 ml polypropylene bottle and analysed within 6 hours on a Seal Analytical QuAAtro Autoanalyser. I measured the silicate concentrations using the following method:

Silicat**e** reacts with ammoniummolybdate to a yellow complex, after reduction with ascorbic acid the obtained blue silica-molybdenum complex was measured at 810nm. Oxalic acid was used to prevent formation of the blue phosphate-molybdenum.

Results:

The concentration of silicate in all samples had a standard deviation of 0.04 µM (0.36%) on an average concentration of 11 µM. This standard deviation equals the standard deviation of the silicate analysis which means that the standard deviation of the bottles is much smaller than 0.36%.

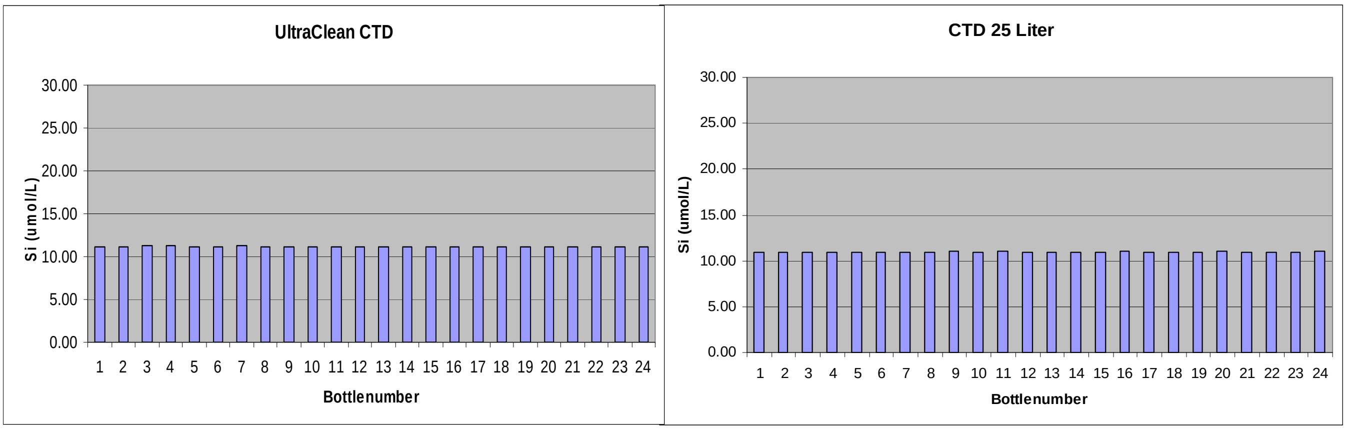


Figure 6: the silicate data (µM) from both frames, average 11 µM, standard deviation 0.04 µM

4.2.2 Dissolved Al

Rob Middag

Dissolved Al was measured directly using shipboard FIA measurements. In a continuous FIA system, the acidified pH 1.8, filtered (0.2 µm) seawater is buffered to pH 5.5. The metals are concentrated on a column which contains the column material aminodiacetid acid (IDA). This material binds only transition metals and not the interfering salts. After washing of the column with ultra pure water (MQ) the column is eluted with diluted acid.

The Al is determined using lumogallion after Brown and Bruland (submitted). Lumogallion is a fluorometric agent and reacts with aluminium. The change in the fluorescence detected by a fluorometer is used as a measure for the dissolved Al concentration.

Preliminary results

The data shows that the new sampling bottles are clean for Al and were all closed at the intended depth.

References

Brown, M.T., Bruland, K.W., 2008. An improved flow-injection analysis method for the determination of dissolved aluminum in seawater. Limnology and Oceanography Methods 6, 87-95.

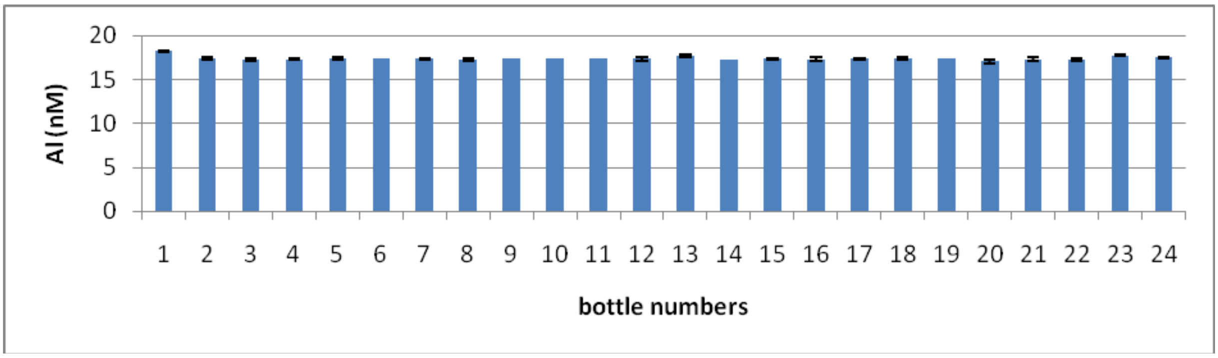


Figure7: Dissolved Al (nM) in each sample bottle. Overall average=17.41 nM, standard deviation =0.22 nM

4.2.3. Dissolved Fe, are the new ultra clean CTD bottles really ultra clean?

Patrick Laan

The main objective during the test cruise from Texel to Scrabster was to test and validate the new ultra clean CTD bottles. After all the mechanical and non trace metal clean tests had been finished we tested the new bottles for their ability to use them for trace metal analysis. During one of the last opportunities of the cruise the bottles were closed all at the same depth and trace metal clean sampled for trace metals.
0.2µm and acidified (pH 1.8) seawater samples were analysed directly on board by an automated Flow Injection Analysis (FIA) after a modified method of De Jong et al. 1998. The seawater was concentrated on a column containing a metal binding resin: aminodiacetid acid (IDA).This material binds only transition metals and not the interfering salts. After washing the column with ultrapure water, the column is eluted with diluted acid. After mixing with luminol, peroxide and ammonium, the oxidation of luminol with peroxide is catalyzed by iron and a blue light is produced and detected with a photon counter.

As indicated in figure 1 concentrations of DFe measured, ranged from 0.957 nM up to 3.13 nM. The standard deviation varied between 0% and 8.5% with a mean of 1.2%. Bottles 2 and 18 were indicated as not clean.

Overall we conclude that the found concentrations in 22 out of the 24 bottles of 1.04 nM +/- 4% indicate that the new ultra clean NIOZ sampler bottles are suitable for trace metal analyses.

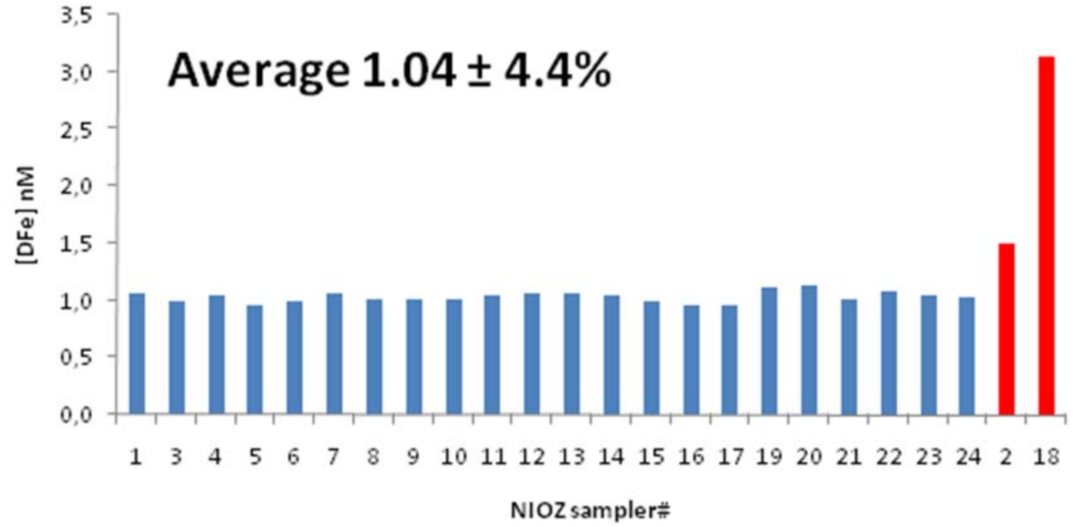


Figure 8: Concentration of dissolved iron per NIOZ sample bottle.

References

Johnson et al., 2007. Developing standards for dissolved iron in Seawater. Eos, Vol 88, n. 11.

De Jong, J.T.M, den Das, J. , Bathman, U., Stoll, M. H.C., Kattner, G., Nolting, R.F., and de Baar, H.J.W. (1998). Dissolved iron at subnanomolar levels in the Southern Ocean as determined by shipboard analysis. Analytica Chimica Acta, 377, 113-124.

4.3 Cost action student training

4.3.1 Report of the cruise from Texel to Scotland

Marco van Hulten

Marco van Hulten at NIOZ helping to assemble the bottles for the UCC frame

Two cruises have been planned for the GEOTRACES project for this year. One will cover the course Reykjavik--Hamilton and the second the course Hamilton--Fortaleza. Before the start of these cruises the equipment had to be tested on a shorter cruise, which I joined. This small cruise started from Texel and the original plan was to go to Reykjavik (Iceland). Here the researchers for the bigger cruises would get on the ship. However, in view of the volcanic activity on Iceland and all the air traffic problems resulting from it, it was decided to go to Scotland instead.

We planned to leave the port at Texel on the 22nd of April but, as often happens with preparations, things got delayed. Added to this, we needed high tide to sail out to sea. This is why we left on Friday the 23rd of April. The North Sea was calm and the sun was shining. It was my birthday, so we ate pie and I got a book which was later signed by everyone on board.

The next day the weather was greyer and I got sea sick in such a way that I did have a chance to participate in or observe any activities on board.

On the third day, April 25, the Very Large and the Ultra Clean sampling systems were let down and pulled up successfully. Both systems contain 24 samplers, each twelve litres in volume. The Ultra Clean is especially useful for the measurement of metal concentrations, because the system is mostly made of plastic to prevent the water from getting into contact with metal.

Leslie and Steven explained the CO2 measurements to me. They measured the alkalinity and DIC (Dissolved Inorganic Carbon), from which concentrations of carbon dioxide, bicarbonate and carbonate can be calculated. The most ingenious I found the measurement of DIC, for which first all ions are converted to carbon dioxide by means of an acid. The resulting liquid is radiated by light with the specific wavelength where carbon dioxide molecules are ionised. Two electrons are measured per molecule. The electric current is integrated by a measurement device. The resulting charge can then be used to calculate the number of mole of carbon dioxide, which is the same as the DIC concentration from the sample.

In the evening there were two lectures; one presented by me about the modelling of trajectories in the ocean, and the other by Gregory about the measurement of concentrations of silicium isotopes.

On the fourth day the sampling systems were let down a bit deeper: about one kilometre. An electric connector of the Very Large sampling system seemed to be leaking. After the replacement of a rubber ring there was no more leakage. In the end we managed to test everything with success.

In the morning of the fifth day, April 27, we sailed into Scrabster, a harbour on the far North of Scotland. Half a dozen people went off board and new scientists went on board for the cruise to Bermuda.

4.3.2 April 26th-27th 2010: Daily diary

by Gregory de Souza

Gregory de Souza sampling for his silicon isotopes from the UC CTD in the clean container.

By the morning of April 26th, RV *Pelagia* was in position for her first deep test station. At 60°06N and 5°45E, we were on the southern slope of the Faroe-Shetland Channel, northwest of Scotland, in about 1000m of water. The day started out overcast and drizzly, with winds of 20m/s according to the ship's new information displays. This being my first cruise, it'd taken me a while to get used to the swell on the North Sea, but on *Pelagia*'s first day beyond the shelf, I realised that I didn't quite have my sea legs yet.

A first test cast to full depth of the ultraclean Titan frame was carried out shortly after 8am; the CTD profile revealed problems with the conductivity and oxygen sensors, and the frame was brought back on deck for repair.

Towards midday, the weather improved slightly, and we were joined by a flock of seagulls that circled the boat expectantly every time a CTD frame was brought on board; imagine their disappointment at the fact that, instead of fish, all we were hauling on board was seawater. As if there weren't enough of that around already.

The last few days since we left Texel have been a good learning experience for me; I've had the chance to see first-hand how the vital cruise data I've so far only received by email (hydrography, nutrients) is actually collected. Especially interesting for me analytically are the highly accurate nutrient analyses by Jan, and the flow-injection analysis of trace metal concentrations that Rob and Patrick will be carrying out on this cruise. I also have a new-found respect for the logistical and technical challenge of sampling at sea; Martin, Edwin and Sven solved a couple of serious technical issues efficiently and with apparent ease.

The Titan, with offending sensor cables replaced, was ready to sample in the early afternoon. All bottled were fired near the bottom, and Jan measured nutrient concentrations from each bottle to check for leaks. The results showed that all bottles were behaving as they should, and so a follow-up cast was carried out to test the cleanliness of the bottles for trace metals, again firing all bottles near the bottom.

The final cast of this rather long test day started after 8pm, collecting a full profile. Steven, Micha and I tapped samples from this cast – I'm excited by the subzero waters at the base of the water column, which seem to be Norwegian Sea overflow waters that would be perfect to complete the Atlantic dataset that forms part of my Ph.D. The nitrogen-overpressure filtering system works perfectly, except for when I connect a tube too loosely, resulting in my first (-0.7°C!) seawater baptism. Live and learn.

As I disembark at Scrabster in the Scottish Highlands the next day, I hear from Rob that the trace-metal test of the Titan shows all bottles to be trace-metal clean. The *Pelagia* is ready for her cruise across the Atlantic.

Appendix 1 Station list

Date	Time	Latitude(deg. min.milli)	Longitude(deg. min.milli)	Device name	Action name	Operation Id	Observation	Station number
26/04/2010	12:19:19	N 60° 5' 10.842''	W 5° 46' 46.168''	CTD UC	Begin	318_CTDUC6		6_2
26/04/2010	12:42:09	N 60° 5' 14.33''	W 5° 46' 51.388''	CTD UC	Bottom	318_CTDUC6		6_2
26/04/2010	13:05:10	N 60° 5' 24.227''	W 5° 47' 5.118''	CTD UC	End	318_CTDUC6		6_2
26/04/2010	13:40:28	N 60° 5' 37.817''	W 5° 48' 43.369''	CTD LV	Begin	318_CTDLV3	FAILED	6_3
26/04/2010	13:46:13	N 60° 5' 38.065''	W 5° 48' 44.91''	CTD LV	End	318_CTDLV3	FAILED	6_3
26/04/2010	15:42:50	N 60° 6' 20.855''	W 5° 49' 31.285''	CTD LV	Bottom	318_CTDLV4		6_4
26/04/2010	16:09:52	N 60° 6' 12.798''	W 5° 49' 30.904''	CTD LV	End	318_CTDLV4		6_4
26/04/2010	17:00:55	N 60° 5' 58.571''	W 5° 47' 45.992''	CTD UC	Begin	318_CTDUC7		6_5
26/04/2010	17:18:23	N 60° 5' 59.478''	W 5° 47' 43.721''	CTD UC	Bottom	318_CTDUC7		6_5
26/04/2010	17:49:09	N 60° 5' 59.507''	W 5° 47' 41.798''	CTD UC	End	318_CTDUC7		6_5
26/04/2010	19:04:02	N 60° 6' 0.356''	W 5° 47' 38.76''	CTD UC	Begin	318_CTDUC8		6_6
26/04/2010	19:21:29	N 60° 6' 6.397''	W 5° 47' 39.894''	CTD UC	Bottom	318_CTDUC8		6_6
26/04/2010	20:00:17	N 60° 6' 13.831''	W 5° 47' 43.321''	CTD UC	End	318_CTDUC8		6_6