Methods (Adapted from the *Shipboard Cruise Report*).

Sampling and sample handling

Seawater samples were collected at depths throughout the water column by a rosette unit equipped with NOEX bottles. The typical vertical spacing between samples was 100 meters down to 1000 meters depth and 250 meters below that. Additional samples were taken closely above the bottom and at 50 meters depth. The surface sample was taken at 10 meters depth. The use of calibrated reversing thermometers guaranteed a vertical accuracy of +/- 2 (?) meters.

Subsamples of 0.6 L were collected from the NOEX bottles according to the procedure outlined by Dickson and Goyet (DOE). No poisoning was applied, however. Analysis of subsamples generally started right away. On several occasions however, subsamples were stored at 4^{o} for up to 12 hours until analysis. Subsamples were kept dark and thermally isolated (and thereby cold) during the period of the analysis runs, which lasted up to 10 hours for the deepest casts. During this period, the last subsamples 'in queue' would however reach temperatures of up to 16 degrees. Given the very low potential for biotic activity in the sampled waters the outlined procedure is considered not to have influenced DIC or Alk values. *Further laboratory studies will need to confirm this*.

Experimental set-up

Two functionally identical machines were used, simply referred to as 'A' and 'B', owned respectively by the Oceanography Dept., Dalhousie Univ., Halifax, Canada and the Royal Netherlands Institute for Sea Research, Texel, The Netherlands.

Machines were set up in the same thermostated lab (which, however, showed considerable temperature swings of up to 8 ^{o}C thereby possibly compromising analysis quality). Operating procedures for both machines were identical in detail. To keep up with the high rate of samples coming in, the machines were mostly running simultaneously.

Insert: statistics on runtime.

Machines differed to some extend in parameters as noise levels, etc.

Use of CRM

Precision of both TA and TCO_2 analyses was determined from duplicate analysis on a number of samples, as well as by the analyses of several replicates of samples (2x, 3x, 4x). The accuracy was set by running certified standards made available by Dr. A. Dickson of the Scripps Institution of Oceanography (USA) after (approximately) every 10 samples. Bottles of CRM were used only once – directly after opening a bottle for the first time, minimizing CO_2 exchange between lab and CRM (which would of course affect TCO_2 measurement). A bottle of CRM would often be used by both machines simultaneously (runs starting at the same moment), doubling the yield from the limited stock of CRM.

TCO_2- and Alk-values of CRM are certified to within XX umol.kg-1 and YY umol.kg-1, respectively. No replicates were run to verify this, again because of the limited amount of CRM available.

Normally, two or three CRM's were run during the analysis of each station. Because the scatter in resulting values for TCO_2 and AT was often within the measurement error, no drift could be detected. The correction factors needed to get the measured TCO_2 and TA values of these CRMs to match the certified values were averaged and applied on the samples from the station.

Total alkalinity analysis

Alkalinity was determined by potentiometric titration of 100 ml samples with 0.1 M HCl.
From the titration curve the total alkalinity (TA) was calculated by subtracting the contribution from other ions present in seawater as determined from the salinity and initial pH of the sample, following DOE.

TCO_2 analysis

Sample analysis for total dissolved inorganic carbon and alkalinity was performed using a VINDTA-3C system (designed by Dr. L. Mintrop, Marine Analytics and Data, Germany). Dissolved inorganic carbon (TCO_2) in a 20 ml sample was determined by coulometry. An automated extraction line takes a volumetric subsample that is acidified with 8.5% phosphoric acid (H_3PO_4) to convert all DIC to $CO_{2(aq)}$. The sample is stripped using nitrogen gas and the carrier gas is led into the titration cell. This cell contains a solution of dimethylsulfoxide, ethanolamine and the colourimetric indicator thymolphtalein. The irreversible reaction of the CO_2 gas with the ethanolamine generates hydroxyethylcarbamic acid which in turn gives a color change of the dark blue indicator. The fading of the color is detected photometrically. During the electrochemical titration the hydroxyethylcarbamic acid is neutralized by OH^- ions. The titration current during the run is integrated over time and, knowing the volume and salinity of the sample, the concentration of DIC per unit mass is computed.

Perhaps departing from regular analysis procedures, we opted for the determination of the coulometer baseline (or 'false counts' or 'background noise') *per run*, rather then a determination of this value on a per-day or per-cast basis. This approach was taken following the observation of variation in baseline values from run to run, a tendency of CRM-runs to give higher baselines than sample-runs and an observed long-term downward trend in baseline values. These variations were of a magnitude that would influence the final result of a run with one or even several umol.kg-1.

The alkalinity analyses take several minutes longer than TCO_2-analyses. Normally during this time, the coulometer would sit idle. However, we changed the program so that this time was used to observe the coulometer noise baseline, by keeping the sample sparging, rather than draining it away, despite it's having been completely stripped of CO_2 already. Per-minute coulometer count increments for the last 7 (or so) minutes were averaged per sample and assumed to represent the run-average noise baseline. This method proved an improvement over the 'standard' one at least for the analysis of CRM, since the standard deviation in measured values dropped from this to that.

Results

CRMs

Typical correction factors (in absolute and relative terms) are given in table 1. TCO2 values can be seen to be quite near the certified value, with the differences probably caused by calibration errors of the two coulometers. (However, no coulometer-swapping was done to verify this).
Two periods are discerned between for the alkalinity measurements on machine 'B', because of a sudden jump in measured values on sept 28th. No explanation can be given for this jump, and measurement quality is compromised, as will be discussed later on.

Replicates

Standard deviations for the results of the several replicates that were analysed are listed in table x. As can be seen, this value is somewhat variable. The highest difference in CT and AT values that was measured is circa 4 umol.kg-1.

Samples

Appendix

Detailed notes on the analysis

During sample introduction, samples were preheated to near the analysis temperature (25oC) in a separate waterbath and by leading them through a stainless steel coil, suspended in a thermostatic bath. Post-coil temperatures were between 24 to 25 degrees, depending on loading speed and sample temperature. This approach eliminates the need for messy sample handling, but also increases the resistance in the sample introduction line. This increases the risk of the potentially gas-oversaturated sample forming bubbles in the sample introduction line. These bubbles were indeed observed at times (but they are also observed when *not* using the pre-heating coil). These bubbles can, if trapped at the 'right' moment, negatively influence the volume of sample situated inside the pipettes, thereby reducing the DIC or Alk value. A back-of-envelope calculation shows, however, that given the small size of the bubbles, the possible error introduced is around the detection limit for the DIC measurement and below that for alkalinity.

Pipette temperature corrections were not applied because of (blabla silly construction)

The main (or even only) difference between the two was that 'A' did not have an automatically controlled CO_2 sparging flow rate, but flow had to be read and manually adjusted. After installing a better pressure reducer on the N_2 bottle during the trials phase of the cruise, flow rate proved very constant. Since not the CO_2 extraction *speed* but rather the extraction *fraction* (which is near 100% after a few minutes, no matter small variations in flow speed) is important for the analysis, this difference is not considered to be of great importance.

(The higher CRM-coulometer-baseline may well be attributed to the CRMs often being the first to be run after the preparation of a new coulometric cell (and subsequent 'junk'-runs)).