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Final Technical Report

Title: Oceanic CO_2 Measurements for the WOCE Hydrological Survey In the Pacific Ocean; Shipboard Alkalinity Analyses During 1991 and 1992

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Summary of Progress

By this grant, our research group contributed titration alkalinity analyses to transects of the WOCE Hydrological Survey during 1991 and 1992. The results have been transmitted to the Carbon Dioxide Information and Analysis Center (CDIAC) of the Department of Energy in a technical data report having two parts:

> Oceanic CO_2 Measurements for the WOCE Hydrographic Survey of the Pacific Ocean, 1990-1991: Shipboard Analyses During 1991 and 1992, Part 1. Alkalinity Measurements on TUNES, Leg 3, 1991
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> Oceanic CO_2 Measurements for the WOCE Hydrographic Survey of the Pacific Ocean, 1990-1991: Shipboard Analyses During 1991 and 1992, Part 2. Alkalinity Measurements on CGC92, Legs 1 and 2, 1992

Part 1 was sent to CDIAC on 14 October, 1994 and Part 2 was sent on 24 October, 1994. Part 1 involves data for a transect from Tahiti to Hawaii along WOCE Line P16C while Part 2 involves WOCE Line P13 from Dutch Harbor, Alaska to Noumea, New Caledonia. The grant also covered the cost of analyses of Dissolved Inorganic Carbon on Cruise CGC92, carried out by the laboratory of Dr. Andrew Dickson of the Scripps Institution of Oceanography. A Final Technical Report on DIC will be sent to CDIAC as soon as possible.

No journal publications have yet been submitted with respect to this grant.

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49

April 14, 1998

Total dissolved inorganic carbon measurements made on WOCE leg P13 (NOAA CGC'92)

Andrew G. Dickson

A summary of the measurements of total dissolved inorganic carbon made on this expedition (Aug 3 – Oct 21, 1992) using the SOMMA instrument. A brief description of how these measurements were made and calibrated has been provided along with a statement of the quality of the measurements. The data themselves have been sent to ORNL CDIAC for archival and distribution.

Table of Contents

Cruise Background[†]

Introduction

This cruise was carried out on the U. S. registered research vessel *R/V John V. Vickers*. This vessel was operated by the University of Southern California together with officers from the NOAA corps.

The goal of the cruise was to carry out a World Ocean Circulation Experiment (WOCE) one-time hydrographic section: the one designated P13 which runs down the line of longitude 165°E from the Kamchatka peninsula to New Caledonia. The cruise was split into two legs for logistical regions

Leg 1
EXPOcode 3220CGC92/1

The chief scientist for Leg 1 of the cruise was Dr. John Bullister from NOAA/PMEL. The *Vickers* left Dutch Harbor (Alaska) on 16 August, 1992 to carry out the cruise, and arrived at Kwajalein (Marshall Islands) on 15 September, 1992.

Leg 1 consisted of 51 stations (Sta. 5-55). The first station on this leg (Station 5) was a test CTD/rosette cast made in the Bering Sea, along the transit from Dutch Harbor to the start of the P13 line near the Kamchatka Peninsula. Sampling of the P13 section began on 21 August 1992 near the 200 meter isobath off Kamchatka. A series of stations were occupied on a southeastward transit down the continental slope and across the Kamchatka Trench. The section turned directly southward at about 51° 30′ N, 165° E, and continued along the 165° E meridian for the remainder of Leg 1. Nominal station spacing was 30 nautical miles from the start of the section to about 40° N. Due to a series of delays during the first part of Leg 1 a decision was made at about 36° N to stretch nominal station spacing for the remainder of Leg 1 (36° N - 10° N) to 40 nautical miles.

Due to concerns about possible structural deformation to Vickers, and concern over failure of a water-tight door to close properly, work on the P13 CTD/rosette section was halted on 9 September 1992 at about 30° N, and *Vickers* was ordered to steam directly to Kwajalein. We were unable to occupy any stations along the emergency transit to Kwajalein.

Leg 2.
EXPOcode 3220CGC92/2

The chief scientist for the second leg of the cruise (Sep 26, 1992 – Oct 21, 1992) was Dr. Bruce Taft from NOAA/PMEL

Vickers remained at the dock in Kwajalein for an extended period of time for evaluation of structural integrity by two marine architects and for repair. *Vickers* left Kwajalein on 26 September 1992 and began steaming back to the break-off point to continue work on the P13 section.

Contact was made with TOGA-COARE investigators (the group scheduled to use Vickers following the completion of the P13 section) to negotiate an extension for

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[†] Portions of this narrative are based on the Chief Scientist's report which is available from the WOCE Hydrographic Program Office at the Scripps Institution of Oceanography: `http://whpo.ucsd.edu/data/onetime/pacific/p13/p13a/p13ado.txt`

Leg 2, which would allow us a reasonable chance to complete the P13 section. After direct negotiations with TOGA-COARE investigators over the revised Vickers schedule, we were unable to come up with a mutually satisfactory agreement. The position held by TOGA-COARE at the end of these negotiations (requiring Vickers to be in port in Noumea on 21 October 1992) did not allow us enough time to complete the WOCE P13 section to even minimum WHP specifications. Since an agreement could not be reached between the 2 programs, the final decision was made by the Director of NOAA's Office of Global Programs, who sent instructions to USC that Vickers should arrive in Noumea on 21 October for TOGA-COARE staging.

With the remaining allocated time, Vickers occupied CTD/rosette stations at a nominal spacing of about 2° from 28° N to 4° N, and closer spacing from 4° N to 4° 30′ S. Lowered ADCP measurements were made on stations between 4 N and 4 S. The section was terminated on 17 October 1992 at 4° 45′ S 164° 0′ E in order to arrive in Noumea by the 21 October deadline. A total of 32 stations (Sta 56-88) were occupied during Leg 2 (one station Sta. 60 was aborted and not included in the listings).

Measurement of Total Dissolved Inorganic Carbon

Introduction

The sampling and analysis for total dissolved inorganic carbon was performed in conjunction with the sampling and analysis for measurements of total alkalinity. The personnel involved were:

Leg 1: Total alkalinity: Peter Guenther (SIO), Guy Emanuele (SIO)
Total carbon dioxide: George Anderson (SIO), Ron Citterman (Battelle, PNL)

Leg 2: Total alkalinity: Andrew Dickson (SIO), Guy Emanuele (SIO)
Total carbon dioxide: Lloraine Bell (SIO), Ron Citterman (Battelle, PNL)

A full depth profile was not sampled at every station occupied. This was because an individual analysis of total dissolved inorganic carbon analysis took about 25 min, and consequently a complete station, together with the various quality control samples and the instrument set-up (new cell, wait for good background) took about 22 hours in all.

Stations sampled for CO_2 measurements

We thus measured as often as we could — approximately every third station when stations had the normal WOCE spacing — and we also analyzed a surface sample taken at the intervening stations. Full profiles are available for the following stations.

Leg 1: 5, 8, 11, 13, 17, 20, 24, 26, 29, 32, 36, 38, 41, 45, 47, 49, 51, 52, 53, 54, 55

Leg 2: 57, 59, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 73, 75, 78, 81, 83, 87

The exact locations of these stations are given in the main WOCE cruise report and data files which are available from the WOCE Hydrographic Program Office:
`http://whpo.ucsd.edu/data/tables/onetime/1tim_pac.htm`

Sampling

The samples for total dissolved inorganic carbon were taken in 500 mL borosilicate glass bottles in accordance with the procedure specified in SOP 1 of the DOE (1994) Handbook of Methods an earlier version of which was available at the time (DOE, 1991). The samples were thus poisoned with mercuric chloride to minimize biological activity prior to analysis.

Two duplicate samples were taken and analyzed for each profile: one in surface water (near the top of the cast) and one in deep water (near the bottom of the cast). These are used to assist in the assessment of the measurement quality.

Analysis technique

The samples were analyzed using a Single Operator Multiparameter Metabolic Analyzer (SOMMA) developed by Mr. Ken Johnson (Johnson *et al.*, 1985; 1987). The procedure using this specific instrument is described in detail in the SOMMA Operating Manual (Johnson, 1991), a description of the procedure is available in the DOE (1994) Handbook of Methods (SOP 2).

The principle behind this analysis is as follows: a known amount of seawater is dispensed into a stripping chamber where it is acidified and purged with an inert gas. The presence of solid carbonates, such as $CaCO_3$, thus constitutes an interference in the method. The amount of CO_2 in the resulting gas stream is determined by absorbing the CO_2 in an absorbent containing ethanolamine and titrating coulometrically the hydroxyethylcarbamic acid that is formed. The pH of the solution is monitored by measuring the transmittance of thymolphthalein indicator at approximately 610 nm. Hydroxide ions are generated by the coulometer circuitry so as to maintain the transmittance of the solution at a constant value. The relevant chemical reactions occurring in the solution are:

$$\mathrm{CO_2 + HO(CH_2)_2NH_2 \rightarrow HO(CH_2)_2NHCOO^- + H^+}$$

and

$$\mathrm{H^+ + OH^- \rightarrow H_2O}\,.$$

The hydroxide ions used are generated at the cathode by electrolyzing water:

$$\mathrm{H_2O} + e^- \rightarrow \tfrac{1}{2}\mathrm{H_2(g) + OH^-}\,,$$

while silver is dissolved at the anode:

$$\mathrm{Ag(s) \rightarrow Ag^+} + e^-\,.$$

The overall efficiency of the coulometric procedure is calibrated using known amounts of CO_2 gas, either from gas loops or from sea water based reference materials.

Order of analyses

The samples were analyzed in the order surface to deep — this gave time for the cooler deep samples to come to room temperature before they were analyzed. However, this means that it is not possible to ascertain from the analytical measurements alone if there means that it is not possible to ascertain from the analytical measurements alone if there is a systematic variation in the calibration with the life of the coulometric cell (see section "Calibration of the analyses" on page 5).

Calibration of the analyses

The calibration of the analyses reported here was problematic. The original plan was to use gas loops to calibrate the coulometer system, and to check the performance of the analyses using certified reference materials (CRM Batch 13 — certified C_T value 2015.13 µmol kg^{-1}). Unfortunately, a post-cruise examination of the results showed that the calibration factor calculated for gas loops was unexpectedly variable; an examination of the calibration factor that would have been calculated from the analyses of the certified reference materials also showed similar variability (equivalent to a standard deviation of measurement of 2.4 µmol kg^{-1}).

A more detailed examination showed that the variability was restricted to those measurements that had been made in the early stages of a cell's lifetime; measurements on gas loops (Figure 1) or on reference materials (Figure 2) made later in the cell's lifetime were much more stable as well as being lower (counts/µmol) than the initial measurements.

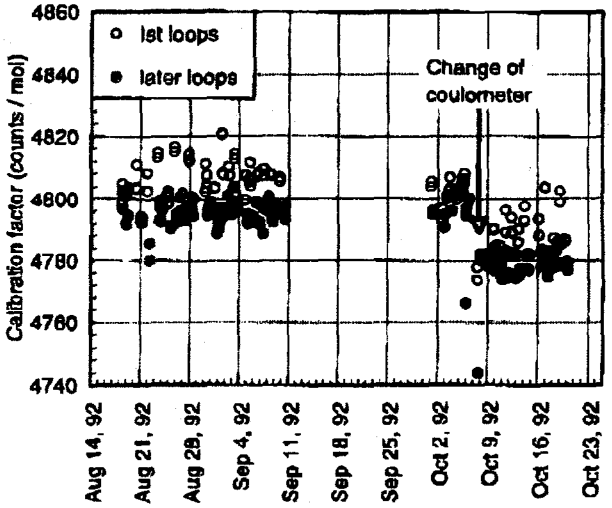

FIGURE 1. Calibration factors from "gas loops" — expressed as counts/µmol.

The reason for this appears to be that the cell was not adequately conditioned prior to being calibrated and used (Ken Johnson, *personal communication*). Consequently, measurements made early in the cell lifetime are suspect. These include all of the initial gas loop calibrations as well as the initial measurement of the reference material. The early measurements — made on water from the upper ocean — may also be somewhat degraded (see "Measurement data quality" on page 6).

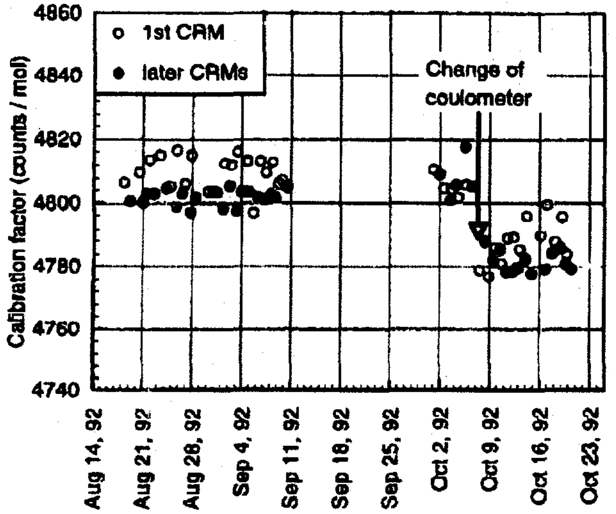

FIGURE 2. Calibration factors from "CRMs" — expressed as counts/µmol.

The calibration approach used to calculate the results presented here was as follows:

- The calibration of an individual coulometer was assumed to remain stable from day to day throughout its period of use. *This assumption reflects the experience of most investigators (see Dickson, 1992) and is also borne out by the measurements from this cruise made later in the cell life (Figure 1 and Figure 2).* Note that a single coulometer unit was used throughout Leg 1, and for part of Leg 2; it was exchanged during Leg 2 on October 7, 1992 prior to measuring samples from Station 65.
- Thus the measurements on reference materials were divided into two groups: one prior to station 65, the other from station 65 to the end of the cruise, and a mean calibration factor was calculated separately for each group of analyses (based on the measurements made on reference materials — later in the cell lifetime).
- This *universal* (coulometer dependent) calibration factor (*i.e.* based on the CRMs) was used to calibrate the measurements made on individual sea water samples.

Measurement data quality

Because of the difficulty in assigning a meaningful calibration to the analyses of total dissolved inorganic carbon made on this cruise, it is hard to assess the data quality of the measurements presented here. Although it is apparent that analyses made "later in the coulometric cell's lifetime" are less variable (Figure 1 & Figure 2), it is less clear when the measuring system "settles down". Thus the measurements that are made early in the cell lifetime are also necessarily suspect (this is discussed in more detail below).

One indication of the potential accuracy of the measurement system is the degree of agreement between the calibration factors based on gas loops and those based on CRMs. The average difference is of the order of 0.1% (Leg 1: 0.14%, Leg 2: 0.06%) thus indicating that the gas loops had the potential of providing an accurate calibration if the cell had been adequately conditioned.

The precision of measurement is harder to assess. Duplicate samples were taken at each full station. These were typically a surface sample (in the top 10 m) and a deep sample (usually the from one of the two deepest Niskin bottles). The duplicates were analyzed with the surface pair being analyzed at the beginning of a run, and the deep pair being split between the beginning and end of a run.

The standard deviation of a single measurement calculated from these duplicates was:

For the "surface" samples (analyzed together) — 1.3 μmol kg^{-1}.
For the "deep" samples (analyzed at the start and end of a run) — 2.0 μmol kg^{-1}.

However, the standard deviation figures are somewhat misleading. The mean difference for the surface samples (first – second) is 0.4 μmol kg^{-1}; that for the deep samples is 1.2 μmol kg^{-1}. This suggests that even during the measurement of these duplicates the "calibration" of the cell is changing in the direction shown in Figure 1 and Figure 2. Hence the measurements on the samples done in the first part of a run — those from the upper ocean — may, on occasion, be biased low by the use of a calibration factor more appropriate to the "later" measurements. An examination of the data on duplicates indicates that the extent of this bias is unlikely to exceed 4 μmol kg^{-1} and may on many occasions be less than that. The measurements on the later (deep) samples would be expected to have a precision that similar to that found for the later CRMs: a standard deviation of 1.1 μmol kg^{-1}, *i.e.* a similar magnitude to that found for those duplicate measurements that were run side-by-side at the beginning of the run.

Data Archival Information

The actual measurements made on this cruise are not included in this document. A copy of the full data set — together with a copy of this document which constitutes the necessary *metadata* — has been sent separately to the Carbon Dioxide Information and Analysis Center (CDIAC) in Oak Ridge, Tennessee where the total carbon measurements will be combined with the total alkalinity measurements and the final WOCE data set and then made available for distribution as a Numeric Data Package.

References

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