INORGANIC CARBON, NUTRIENT, AND OXYGEN DATA FROM THE R/V *RONALD H. BROWN* REPEAT HYDROGRAPHY CRUISE IN THE ATLANTIC OCEAN: CLIVAR CO2 SECTION A16N_2003A (4 JUNE–11 AUGUST, 2003)

Contributed by
E. Peltola,[1] R. Wanninkhof,[1] R. Feely,[2] R Castle,[1] D. Greeley,[2] J.-Z. Zhang,[1]
F. Millero,[3] N. Gruber,[4] J. Bullister,[2] and T. Graham[3]

[1]Atlantic Oceanographic and Meteorological Laboratory, NOAA, Miami, FL
[2]Pacific Marine Environmental Laboratory, NOAA, Seattle, WA
[3]Rosentiel School of Marine and Atmospheric Research, Miami University, Miami, FL
[4]University of California Los Angeles, Los Angeles, FL

Prepared by
Alex Kozyr
Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
Oak Ridge, Tennessee, USA

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ABBREVIATIONS AND ACRONYMS

AOML	Atlantic Oceanographic and Meteorological Laboratory
BNL	Brookhaven National Laboratory
CCSP	Carbon Cycle Science Program
CDIAC	Carbon Dioxide Information Analysis Center
CFC	chlorofluorocarbon
CLIVAR	Climate Variability (Program)
CO_2	carbon dioxide
CRM	certified reference material
CTD	conductivity, temperature, and depth sensor
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
EXPOCODE	expedition code
fCO_2	fugacity of CO_2
GCOS	Global Climate Observing System
GCRP	Global Change Research Program
GOOS	Global Ocean Observing System
JGOFS	Joint Global Ocean Flux Study
LDEO	Lamont-Doherty Earth Observatory
MLR	multilinear regression
NDP	numeric data package
NDIR	nondispersive infrared analyzer
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
ORNL	Oak Ridge National Laboratory
pCO_2	partial pressure of CO_2
PMEL	Pacific Marine Environmental Laboratory
QA	quality assurance
QC	quality control
RSMAS	Rosentiel School of Marine and Atmospheric Science
R/V	research vessel
SIO	Scripps Institution of Oceanography
SOMMA	single-operator multi-parameter metabolic analyzer
SST	sea surface temperature
TALK	total alkalinity
TCO_2	total inorganic carbon
UCI	University of California, Irvine
UW	University of Washington
WHP	WOCE Hydrographic Program
WOCE	World Ocean Circulation Experiment

ABSTRACT

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This report presents methods and analytical and quality control procedures for nutrient, oxygen, and inorganic carbon system parameters performed during the A16N_2003a cruise, which took place from June 4 to August 11, 2003 aboard NOAA Ship R/V *Ronald H. Brown* under auspices of the National Oceanic and Atmospheric Administration (NOAA). The first hydrographic leg (June 19–July 10) was from Reykjavik, Iceland, to Funchal, Madeira, Portugal along the 20°W meridian, and the second leg (July 15–August 11) continued operations from Funchal, Portugal to Natal, Brazil, on a track southward and ending at 6°S, 25°W. The research was the first in a decadal series of repeat hydrography sections jointly funded by NOAA and the National Science Foundation (NSF) as part of the CLIVAR/CO_2/hydrography/tracer program. Samples were taken from up to 34 depths at 150 stations.

The data presented in this report includes the analyses of water samples for total inorganic carbon (TCO_2), fugacity of CO_2 (fCO_2), total alkalinity (TALK), pH, nitrate (NO_3), nitrite (NO_2), phosphate (PO_4), silicate (SiO_4), and dissolved oxygen (O_2).

The R/V *Ronald H. Brown* A16N_2003a data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center (CDIAC). The NDP consists of the oceanographic data files and this printed documentation, which describes the procedures and methods used to obtain the data.

Keywords: carbon dioxide, total CO_2, total alkalinity, pH, fugacity of CO_2, carbon cycle, coulometry, potentiometry, hydrographic measurements, CLIVAR, Atlantic Ocean

1. BACKGROUND INFORMATION

The cruise of research vessel (R/V) *Ronald H. Brown* along section A16N from Reykjavik, Iceland, to Natal, Brazil, was the first in a series of repeat hydrography cruises to measure decadal changes in circulation, heat and fresh water budgets, and carbon inventory in the ocean. The cruises repeat a subset of the World Ocean Circulation Experiment Hydrographic Program (WHP) and Joint Global Ocean Flux Study (JGOFS) lines occupied in each major ocean basin in the 1990s.

The WOCE/WHP program is driven by the need to monitor the changing patterns of carbon dioxide (CO_2) in the ocean and provide the necessary data to support continuing model development that will lead to improved forecasting skills for oceans and global climate. During the 1990s, the WOCE/JGOFS survey provided a full-depth baseline data set against which to measure future changes. By integrating the scientific needs of programs requiring measurement of the full water column, major synergies and cost savings are achieved. These measurements are of importance both for major research programs, such as Climate Variability (CLIVAR) and the U.S. Global Carbon Research Project (GCRP) Carbon Cycle Science Program (CCSP), and for operational activities such as the Global Ocean Observation System (GOOS) and the Global Climate Observing System (GCOS). As outlined in the program documentation one component of a global observing system for the physical climate/CO_2 system should include periodic observations of hydrographic variables, CO_2 system parameters, and other tracers. The large-scale observation component of CCSP has a need for systematic observations of the invasion of anthropogenic carbon in the ocean that is superimposed on a variable natural background. The five topical areas addressed by the CO_2/CLIVAR repeat hydrography program are

1. carbon system studies;
2. heat and freshwater storage and flux studies;
3. deep and shallow water mass and ventilation studies;
4. calibration of autonomous sensors; and
5. data for model calibration.

The *Ronald H. Brown* cruise consisted of a transit leg from Charleston, South Carolina, USA to Reykjavik, Iceland, during which limited surface-water observations were taken. The first hydrographic leg was from Reykjavik to Funchal, Madeira, Portugal along the 20°W meridian; the second leg continued operations from Funchal, Portugal to Natal, Brazil, on a track southward, ending at 6°S, 25°W (see Fig. 1.1).

This data report focuses on the measurements of total inorganic carbon (TCO_2), fugacity of CO_2 (fCO_2), total alkalinity (TALK), pH, nitrate (NO_3), nitrite (NO_2), phosphate (PO_4), silicate (SiO_4), and dissolved oxygen (O_2).

The methodology, instrumentation, and standardization of these parameters improved significantly during the WOCE/JGOFS era. Notable developments include release of manuals detailing the analytical methods and operating protocols (DOE 1994). Certified reference materials (CRMs) are now available for TCO_2 and TALK, which are run interspersed with samples to determine calibration offsets. For this cruise the TALK values were adjusted to account for the small difference between the CRMs run at sea and the certified value determined at Scripps Institution of Oceanography (SIO). For TCO_2 there were problems with the gas loop calibrations that were attributed to inaccurate temperature sensors. The reference materials were therefore used as primary calibration for both TCO_2 and TALK.

Instrumentation also improved in the last decade. Alkalinity measurements can be done with better precision through automation and close checks of the response of electrodes. Burettes are independently calibrated, and the preparation of titrant (hydrochloric acid) undergoes improved quality control and standardization (Millero et al. 1998). Measurement of pH is now done with extreme precision with spectrophotometric methods (Byrne and Breland 1989). The TCO_2 measurements are done by

coulometry, a precise integrative method. During the A16_2003a cruise we utilized two single-operator multiparameter metabolic analyzers (SOMMAs) (Johnson et al. 1999) for analyses, which facilitated a sample throughput of up to 80 samples per day. The fCO_2 measurements were done with an equilibration system described in Wanninkhof and Thoning (1993). For this cruise data reduction and calculation routines were changed. Comparisons of the data with those from a cruise along a similar transect in 1993 show an appreciable bias between results, as is detailed in the section describing the pCO_2 analyses. Oxygen measurements were performed by Winkler titrations (Carpenter 1965) with photometric endpoint detection (Friederich, Sherman, and Codispoti 1984). The titrator worked well, but there were issues with errors in bottle volumes and problems with pipettes used to generate standard curves. Extensive post-cruise troubleshooting and bottle volume redetermination were necessary to reduce the data.

The data underwent careful quality assurance and quality control (QA/QC) both during and after the cruise. The precision of the measurements was determined from duplicate sampling and comparison of data from deep water, where little variability is expected. Outliers in the data were flagged based on several methods utilizing prior knowledge of the trends and known relationships between parameters. Depth profiles for each parameter were scrutinized for outliers. When deviations

Fig. 1.1. Cruise track for the Atlantic Ocean A16N_2003a cruise in June–August 2003.

were observed, other parameters were assessed to determine whether they showed deviations as well. Inorganic carbon system parameters were linked through physical and chemical properties; if two of the four parameters are measured, the other two can be calculated, provided that the silicate composition, the phosphate composition, the temperature, and the salinity of the sample are known. These so-called overdeterminations or internal consistency calculations were used to assess the difference between calculated and measured values. When the difference between the measured TALK and the TALK calculated from TCO_2 and pH or fCO_2 exceeded 10 μmol/kg, the three parameters were scrutinized and compared with other parameters to assess whether the datum should be labeled as questionable. Other techniques, described in detail below, include regional multilinear regressions (MLR) between the inorganic carbon parameters and physical and chemical parameters known to correlate with them [for instance, $TCO_2 = f(T, S, AOU, Si, PO_4)$]. Again the differences between measured and calculated parameters were inspected. Finally, the parameters were plotted against latitude for narrow depth intervals. Since changes along depth horizons are usually gradual, anomalies can be easily spotted and flagged.

This report describes procedures and methods for hydrographic measurement and the analytical procedures, calculations, and assessment of precision for nutrient, oxygen, TCO_2, TALK, fCO_2, and pH measurements. A description of the QA/QC methods based on internal consistency of these parameters and the MLR technique is also provided.

2. DESCRIPTION OF THE EXPEDITION

2.1   R/V *Ronald H. Brown:* Technical Details and History

The National Oceanic and Atmospheric Administration (NOAA) ship R/V *Ronald H. Brown*, a state-of-the-art oceanographic and atmospheric research platform, is the largest vessel in the NOAA fleet. With its highly advanced instruments and sensors, R/V *Ronald H. Brown* travels worldwide supporting scientific studies to increase our understanding of the world's oceans and climate. Commissioned on July 19, 1997, in its home port of Charleston, South Carolina, *Ronald H. Brown* has sailed in the Pacific, Atlantic, and Indian Oceans. The ship was named in honor of former Secretary of Commerce Ronald H. Brown, who was killed in a plane crash on April 3, 1996, while on a trade mission to Bosnia. R/V *Ronald H. Brown* is operated by NOAA Marine and Aviation Operations and carries a complement of 6 NOAA Corps officers, 20 crew members, and a maximum of 33 scientists. Table 2.1 provides a detailed description of the ship.

Table 2.1. Specifications of R/V *Ronald H. Brown*

Designer	VT Halter Marine, Inc.
Builder	VT Halter Marine, Inc., Moss Point, Mississippi
Launched	May 30, 1996
Delivered	April 18, 1997
Commissioned	July, 19, 1997
Hull number	R104
Call letters	WTEC
Home port	Charleston, South Carolina
Length	83.5 m (274 ft)
Breadth (molded)	16.0 m (52.5 ft)
Draft, maximum	5.2 m (17.0 ft)
Depth to main deck	8 m (26.5 ft)
Displacement	3,250 tons
Maximum speed	15 kn
Cruise speed	12 kn
Range	11,300 nm at 12 kn speed plus 30 days on station
Total crew and scientists	58
Maximum cruise duration	60 days
Science quarters	Main lab: 1,730 ft^2
	Electronics/computer lab: 720 ft^2
	Wet lab: 230 ft^2
	Hydro lab: 700 ft^2
	Biochemical lab: 720 ft^2

2.2   R/V *Ronald H. Brown* A16N_2003a Cruise Information

Ship name	Ronald H. Brown
EXPOCODE	33RO200306_01_02
WOCE section	A16N
Ports of call	Reykjavik, Iceland, Funchal, Madeira, Portugal and Natal, Brazil
Dates	June 4–August 11, 2003
Funding support	NOAA, NSF
Chief scientists	Dr. John L. Bullister, NOAA/PMEL
	Dr. Niki Gruber, UCLA

Parameters measured, institution, and responsible investigators

Parameter	Institution	Responsible personnel
CTD, salinity, CTD/O_2	PMEL	G. Johnson
Nutrients	PMEL, AOML	C. Mordy, J.-Z. Zhang
Oxygen	AOML	J.-Z. Zhang
CFCs	PMEL, UW	J. Bullister, M. Warner
Tritium, Helium	LDEO	P. Schlosser
TCO_2, fCO_2	AOML, PMEL	R. Wanninkhof, R. Feely
TALK, pH	RSMAS/UM	F. Millero
DOC	RSMAS/UM	D. Hansell
^{14}C, ^{13}C	UCI	E. Saltzman

Participating institutions

PMEL	Pacific Marine Environmental Laboratory
AOML	Atlantic Oceanographic and Meteorological Laboratory
LDEO	Lamont-Doherty Earth Observatory
RSMAS/UM	Rosentiel School of Marine and Atmospheric Science, University of Miami
UCI	University of California, Irvine
UW	University of Washington

3. DESCRIPTION OF VARIABLES AND METHODS

3.1 Nutrient and Oxygen Measurements

The analytical method for determining dissolved oxygen in seawater during the A16N_2003a cruise was based on automated Winkler titration as described by Culberson et al. (1991), and Williams and Jenkinson (1982) and modified by Friederich, Codispoti, and Sakamoto (1991). Dissolved oxygen samples were withdrawn from 10-L Niskin bottles to 145-mL Pyrex brand iodine flasks (Corning 5400, Corning, New York, USA). The exact volume of each flask at room temperature had been gravimetrically calibrated with its ground glass stopper following standard procedures (DOE 1994; WHP Operations and Methods 1991). Quantities of 1 mL of manganese chloride reagent and 1 mL of alkaline iodide reagent were added to each sample in the iodine flasks, and then the stopper was placed in the bottle neck. The bottles were shaken vigorously for about 1 min to completely fix oxygen with manganese hydroxide [$Mn(OH)_3$]. In this method, dissolved oxygen in the sample reacts with $Mn(OH)_3$ to form $Mn(OH)_3$ precipitate. Particulate $Mn(OH)_3$ dissolves upon the acidification, and the resulting Mn^{3+} ions oxidize iodide to iodine in acidic solution. The liberated iodine complexes with excess iodide, forming I_3^-, and the latter is titrated with a sodium thiosulfate solution that is standardized by a primary standard potassium iodate. The complex I_3^- has a maximum absorbance at 352 nm; this change in absorbance at 352 nm is used to detect the end point. A custom-built automated oxygen titrator with MS DOS interfacing software was used to determine dissolved oxygen concentrations in the samples.

A total of 5011 seawater samples were taken from 150 stations and analyzed for dissolved oxygen concentrations. At the beginning of cruise, a test conductivity, temperature, and depth (CTD) cast was made by sampling 20 Niskin bottles from same depth (170 m). Analysis of these samples indicated a precision of 0.3 µmol/L. Throughout the cruise duplicate samples from the same Niskin bottle were collected at each station to estimate the precision of the overall measurements (sampling and analysis). Analyses of 300 replicate samples indicated that the precision of the shipboard automated Winkler titration was 0.29 µmol/L including all outliers, and 0.24 µmol/L excluding the outliers. An analysis of outliers indicated that most outlying values in the duplicate analysis were due to errors in the volumes of oxygen bottles; a minority were due to problems with Niskin bottles or sampling error. The outliers in vertical profiles of oxygen were also used to identify the bottles that might have errors in volumes. A total of 33 sample bottles were recalibrated; 11 proved to have volume errors greater than 0.3 mL. These accounted for about 5% of the sample bottles used during the A16N_2003a cruise. The volumes of the oxygen bottles identified as questionable were recalibrated after the cruise, and dissolved oxygen concentrations were recalculated for those samples using correct volumes.

At the beginning of leg 2 of the cruise (from stations 72 to 79) a problematic automatic pipette was used to deliver the KIO_3 standard solution for standardization of thiosulfate solution in batch number 14. An unusually high slope was observed, and this pipette was not used in subsequent analyses. A shipboard and post-cruise comparison indicated that there was an error in volume delivery of this automatic pipette. Consequently, dissolved oxygen concentrations from stations 72 to 79 were corrected for errors in volume delivery of iodate solution by this automatic pipette. The correction factor (1.0153) was estimated on the basis of the post-cruise recalibration of the pipette and was applied to data from station 72 to 79.

Since the Dosimat titrators have demonstrated high precision and accuracy in volume delivery of titrants (0.05 and 0.2%, respectively, at delivery of 10 mL solution), we recommend use of a Dosimat or a similar positive-displacement burette to quantitatively dispense the iodate standard solution during future cruises. This procedure can improve the accuracy of shipboard oxygen analysis.

Nutrient samples were collected from Niskin bottles in acid-washed 25-mL linear polyethylene bottles after at least three complete seawater rinses and analyzed within 2 hours of sample collection. Measurements were made in a temperature-controlled (20 ± 2°C) bioanalytical laboratory aboard the R/V *Ronald H. Brown*. Concentrations of nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and silicic acid

(H_4SiO_4) were determined using a modified Alpkem Flow Solution Auto-Analyzer coupled with a modified RFA 301 autosampler. Sample and wash time for the auto sampler were set at 120 and 5 seconds, respectively.

Nitrite content was determined by diazotizing the samples with sulfanilamide and bonding with N-1 naphthyl ethylenediamine dihydrochloride to form an azo dye. The color produced is measured at 540 nm (Zhang, Ortner, and Fischer 1997). Samples for nitrate analysis were passed through a laboratory-crafted cadmium column (Zhang, Fischer, and Ortner 2000) to reduce nitrate to nitrite. Total nitrite, mostly from reduction of nitrate with a small amount of nitrite present in the original samples, was then determined as described above. Nitrate concentrations in seawater samples were calculated by difference.

The amount of phosphate in the samples was determined by reacting the samples with molybdenum (VI) in an acidic medium to form a phosphomolybdate complex. This complex was subsequently reduced with hydrazine at a temperature of 55°C to form phosphomolybdenum blue (Zhang, Fischer, and Ortner 2001). An AAII detector with an 880-nm filter was used to measure the absorbance during the cruise.

Silicic acid in the samples was analyzed by reacting samples with molybdate in a acidic solution to form β-molybdosilicic acid. The β-molybdosilicic acid was then reduced by ascorbic acid to form molybdenum blue (Zhang and Berberian 1997). The absorbance of the molybdenum blue was measured at 660 nm.

The low-nutrient water used for the preparation of working standards, determination of blank, and the wash between samples was filtered seawater obtained from the surface of the Gulf Stream. Stock standard solutions were prepared by dissolving high-purity standard materials (KNO_3, $NaNO_2$, KH_2PO_4 and Na_2SiF_6) in deionized water. Working standards were freshly made at each station by diluting the stock solutions in low-nutrient seawater. Standardizations were performed prior to each sample run with working standard solutions. Two or three replicate samples were collected from a Niskin bottle that tripped at the deepest depth at each cast. The relative standard deviation from the results of these replicate samples was used to estimate the overall precision for the sampling and analytical procedures. The precision of analyses was 0.08 μmol/kg for nitrate, 0.01 μmol/kg for phosphate, and 0.1 μmol/kg for silicic acid, respectively.

3.2 Total Inorganic Carbon Measurements

Samples were drawn from the Niskin bottles into cleaned, precombusted 540-mL Pyrex bottles using Tygon tubing according to procedures outlined in DOE's handbook of methods for CO_2 analysis (DOE 1994). Bottles were rinsed once and filled from the bottom, overflowing half a volume. Care was taken not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5-mL headspace; and 0.2 mL of saturated $HgCl_2$ solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease and were stored at room temperature for a maximum of 12 hours prior to analysis.

The TCO_2 analytical equipment was set up in a seagoing laboratory van. The analysis was done by coulometry with two analytical systems (AOML-1 and AOML-2) used simultaneously on the cruise. Each system consisted of a coulometer (UIC, Inc.) coupled with a SOMMA inlet system developed by Ken Johnson, formerly of Brookhaven National Laboratory (Johnson 1992; Johnson, King, and Sieburth 1985; Johnson et al. 1987, 1993). In the coulometric analysis of TCO_2, all inorganic carbon is converted to CO_2 (gas) by the addition of excess hydrogen ions (acid) to the seawater sample, and the evolved CO_2 gas is swept into the titration cell of the coulometer with compressed nitrogen, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated OH^-. Carbon dioxide is quantified by integrating the total charge required to achieve this.

The coulometers were calibrated by injecting aliquots of pure CO_2 (99.995%) by means of an eight-port valve outfitted with two sample loops that had been calibrated by Kelly Brown, CCN Consulting (Wilke, Wallace, and Johnson 1993). Due to large temperature variations of the gas loops, the calibration

factors obtained from gas loop measurements were of poor quality. Instead of using an average of the small and large loop values as recommended in DOE (1994), we used a constant value for each analyzer throughout the entire cruise. The constant calibration value used for AOML-1 was 1.00532 and for AOML-2 1.00650. The CO_2 gas volumes bracketed the amount of CO_2 extracted from the water samples for the two AOML systems. All TCO_2 values were corrected for dilution by 0.2 mL of $HgCl_2$ used for sample preservation. The correction factor used for dilution was 1.00037. A correction was also applied for the offset from the Certified Reference Material (CRM) Batch 59, supplied by Dr. A. Dickson (SIO). This correction was applied for each cell using the CRM value obtained for the cell at the beginning. To check the stability of the coulometer and coulometer solutions, the CRMs were measured at the beginning, middle, and end of each coulometer cell solution. The coulometer cell solution was replaced after 25 mg of carbon was titrated, typically after 9–12 hours of continuous use. Sample titration times were 9–16 minutes.

Replicate seawater samples were taken from Niskin sample bottles at the surface, at 1000 m, and at the sea bottom and were run at different times during the cell. The first replicate of the surface water was used at the start of the cell with fresh coulometer solution; the second surface replicate and the first one of the 1000 replicates were run in the middle of the cell after about 12 mg of carbon were titrated. The second one of the 1000 m replicates and the first one of the bottom replicates were run at the end of the cell after about 25 mg of carbon were titrated, while the second one of the bottom replicate samples was run using a new coulometer cell solution. No systematic difference between the replicates was observed. The trends do not suggest any systematic dependency of results with amount of carbon titrated for a particular cell. The results of the duplicate samples are shown in Fig. 3.1 and Table 3.1.
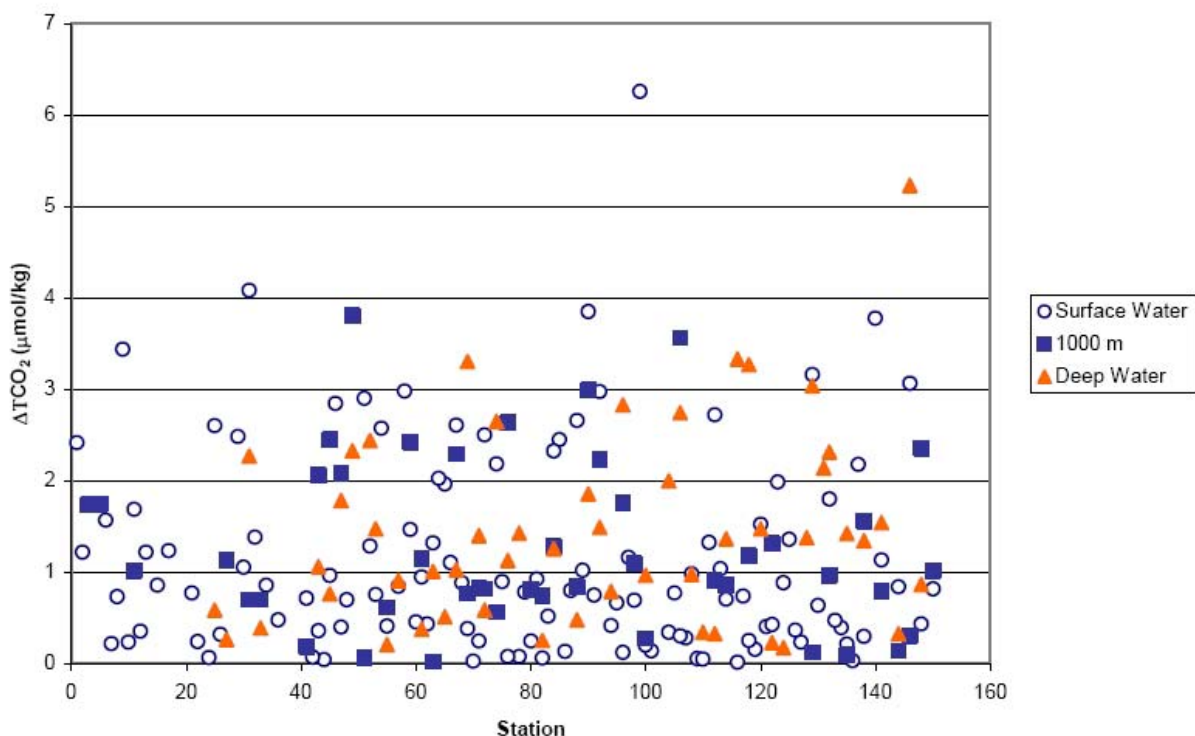

Fig. 3.1. Results of the duplicate TCO_2 samples collected during the R/V *Ronald H. Brown* cruise along the Atlantic Ocean section A16N_2003a.

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Table 3.1. TCO$_2$ duplicate measurement statistics

Measurement method	Av.	Std. dev.	No.
Duplicate samples measured back-to-back	0.8	0.80	94
One duplicate measured in the beginning; the other in the middle of the cell	1.3	0.94	39
One duplicate measured in the middle; the other at the end of the cell	1.2	0.57	13
One duplicate measured in the beginning; the other, at the end of the cell	1.3	1.27	8
Duplicates run on the same instrument but on different cells	1.4	0.86	56
Duplicates run on different instruments	0.7	0.42	3
Duplicates measured in the beginning of the cell, but not back-to-back	—	—	0
Duplicates measured in the middle of the cell, but not back-to-back	1.3	1.01	6
Duplicates were measured in the end of the cell, but not back-to-back	1.0	0.30	3
Total no. of measurements			286
Measurements deleted[a]			64
Measurements used			222

[a] Measurements that were two standard deviation removed from the mean were omitted from the statistics.

The concentration of TCO$_2$, designated as [CO$_2$], in the samples was determined according to

$$[CO_2] \;=\; Cal.\,factor \;\times\; \frac{(Counts - Blank \times Run\,time) \times K\,\mu mol/Count}{Pipette\,volume \times Density\,of\,sample}\;, \qquad (3.1)$$

where *Cal. factor* is the calibration factor fixed for this cruise because of the malfunctioning of the gas loops, *Counts* is the instrument reading at the end of the analysis, *Blank* is the counts per minute determined from blank runs performed at least once for each cell of the solution, *Run time* is the length of coulometric titration (in minutes), and *K* is the conversion factor from counts to μmol, which is dependent on the slope and intercept relation between instrument response and charge. For a unit with an E_{cal} slope of 1 and an intercept of 0, the conversion factor is 2.0728×10^{-4}.

The blank values for AOML-1 were in the range of 12.0 to 33.3 counts/min, with an average value of 19.6 counts/min and a standard deviation of 6.8 counts/min. For AOML-2 they were in the range of 12.0 to 30.0 counts/min, with an average value of 21.7 counts/min and a standard deviation of 6.1 counts/min.

The pipette volume was determined by taking aliquots of distilled water at a known temperature from the volumes prior to the cruise. The weights with the appropriate densities were used to determine the volume of the pipettes (AOML-1: 28.726 cm^3 @ 19.96°C, AOML-2: 22.623 cm^3 @ 22.63°C).

Calculations of pipette volumes, density, and final CO$_2$ concentrations were performed according to procedures outlined in the DOE CO$_2$ handbook (DOE 1994).

3.3 Fugacity of CO_2 Measurements

The fugacity of CO_2 ($fCO2$) was measured on the A16N-2003a cruise at a constant temperature of 20°C by equilibrating a 500-mL water aliquot in a volumetric flask with a closed headspace. The headspace is circulated through a nondispersive infrared detector that measures both CO_2 and water vapor levels. The analytical instrumentation is detailed in Wanninkhof and Thoning (1993) and is the same as the setup used in the N.Atl-93 cruise that occupied the same cruise line in 1993 (Castle et al. 1998).

The system is patterned after that of Chipman, Marra, and Takahashi (1993) with modifications as presented in Wanninkhof and Thoning (1993). In short, a 500-mL water sample is equilibrated at ambient pressure with an 80-mL headspace in a thermostatted volumetric flask. The headspace is circulated through a nondispersive infrared analyzer (NDIR), LICOR model 6262. Upon equilibration the circulation flow is stopped, and 30 readings of water vapor content and CO_2 content in the cell are taken over a 30-second interval and averaged. The system is a dual-channel system where one equilibration occurs while circulating through the NDIR and a second flask is equilibrated offline. Once the first sample is analyzed, the second flask is switched in line with the NDIR, and the gas in the NDIR is equilibrated with the second flask content. The second equilibration phase through the NDIR takes less time, as a large part of the headspace has already been equilibrated offline. The two-channel configuration decreases the total analysis time to about 20 min for two samples.

The system is calibrated after every eight samples with six gaseous standards traceable to the manometrically determined values of C. D. Keeling of SIO. The mole fractions of the standards used during the A16N_2003a cruise were as follows:

Tank number	Mole fraction (ppm)
CA05989	378.7
CA05980	792.5
CA05984	1036.9
CA05940	1533.7
CA05988	593.6
CA05998	205.1

The standards were also used as the headspace gas for the equilibration. Since the mole fractions of the gases in the headspace prior to equilibration are known, the small perturbation of fCO_2 in the water during the equilibration process can be accounted for quantitatively. The headspace gas is selected such that it is close the anticipated water value, thereby minimizing the correction.

The calculation of fCO_2 involves several steps, including the conversion of the NDIR output to an equivalent dried mole fraction of CO_2, the correction for the perturbation of fCO_2 in water by equilibration, and the small adjustment from the measurement temperature to 20°C. For the reduction of the A16N-2003a fCO_2 we made an important adjustment in procedures. On previous cruises, the calibration of the samples that were run at 100% water vapor pressure (@ 20°C) to the dry standards was done through an empirical algorithm created by running standards both wet and dry. For this cruise we relied on the internal correction from wet to dry mole fraction of CO_2 provided by the LI-COR 6262. This change is based on testing by our group and other investigators that showed that the correction provided by the instrument is of high quality and subject to less uncertainty than our empirical corrections. Since this is a fundamental change in our procedures, we describe the old and new routine in detail below, including comparison of the results.

The correction from detector output to (dry) mole fraction of CO_2, xCO_2 in the headspace was previously done by measuring the voltage output of the CO_2 and H_2O channel. An empirical algorithm between dry standards and standards saturated with water vapor at 20°C was created in the form

$$MVCO_2(dry) = MVCO_2(wet) + A + B \times MVCO_2(wet) + C \times [MVCO_2(wet)]^2 , \qquad (3.2)$$

where MV is the millivolt output of the CO_2 channel and $MVCO_2$ (wet) is the millivolt value measured for the equilibrated headspace of the sample. From this algorithm the (water-saturated) headspace gas is corrected to the dry state such that the samples can be directly related to the standard. The next step is to convert the $MVCO_2$(dry) of the sample to an xCO_2 by creating a curve of $MVCO_2$(dry) versus xCO_2 using the standards preceding and following the samples. For each sample the three standards closest to the samples are selected and a second-order polynomial is created of $MVCO_2$ versus xCO_2 by averaging the appropriate standards preceding and following the sample. The second-order polynomial is then used to calculate the xCO_2 of the sample.

Following this step the fCO_2 in the headspace is calculated according to

$$fCO_2 = xCO_2 \, (1 - pH_2O) \times 0.9966 \, , \tag{3.3}$$

where pH_2O is the water vapor pressure @ 20°C (= 0.0226 atm) and 0.9966 is the conversion factor from pCO_2 to fCO_2 @ 20°C.

The next step is the correction for change in fCO_2 in the water sample due to exchange of CO_2 with the headspace during equilibration. This step is accomplished by using the mass balance criterion that the total amount of carbon in the headspace and water is conserved and by using the fact that the TALK remains unchanged during equilibration. The TCO_2 of the sample (determined independently) and the headspace gas concentration prior to equilibration along with the volume of water and headspace are used to calculate the total amount of carbon in the system. From the change in headspace CO_2 before versus after equilibration, the change the TCO_2 in the water can then be determined. From this change and the TALK (calculated from TCO_2 and fCO_2 after equilibration), the fCO_2 in the water before equilibration can then be determined.

The final step is to correct the fCO_2 from analysis temperature to 20°C. The water samples were always equilibrated within 0.1°C of 20°C such that this correction is less than 0.4% of the value. The correction for perturbation of fCO_2 in the water during equilibration and the temperature correction to 20°C are performed using the carbonate dissociation constants and the temperature dependence of the constants and the calculation routines described in Peng et al. (1987).

For A16N_2003a the correction from the moist gas of the sample to an equivalent dry concentration was performed utilizing the internal correction routine built into the Li-6262 analyzer. This internal algorithm has been extensively checked by others and our tests also showed that the correction was robust. The important advantage of this internal correction is that in our previous data reductions we assumed that the algorithm between wet and dry created in laboratory tests before the cruise or after the cruise does not change appreciably over time. This has proven to not always be the case. Secondly, the water vapor level measured during the standard runs can be appreciable despite an absence of water vapor in the compressed gas standards, since it takes a long time for the water vapor introduced by the equilibration of the samples to be flushed from the system. Therefore, we see a decreasing trend of water vapor level when the six standards are run consecutively (Fig. 3.2).

The modified data reduction routine uses the xCO_2(dry) calculated by the detector for both standards and samples. A second-order polynomial fit is created between the actual mole fraction of CO_2 in the standard and the instrument value. This standardization accounts for instrument drifts over time. The detector was zeroed and spanned for CO_2 every day, while the water vapor channel was spanned just before the first leg and before the second leg. Standardizing the water vapor channel is difficult because of the "stickiness" of the water vapor, which leads to lags and very slow response times. A polynomial is created for the three standards closest to the sample by averaging the pertinent standards before and after taking the sample. The other steps of correcting for small temperature deviations of the water bath from 20°C and correction to fCO_2 prior to equilibration are identical to the procedures outlined above.

The new correction routine results in small differences in values for calculated fCO_2 compared to the previous data reduction routine. Table 3.2 shows a comparison in values for station 45 using the different methods. The values using the new reduction routine are systematically about 2 μatm lower than those obtained through the old reduction method. The table also gives the results of two different water vapor
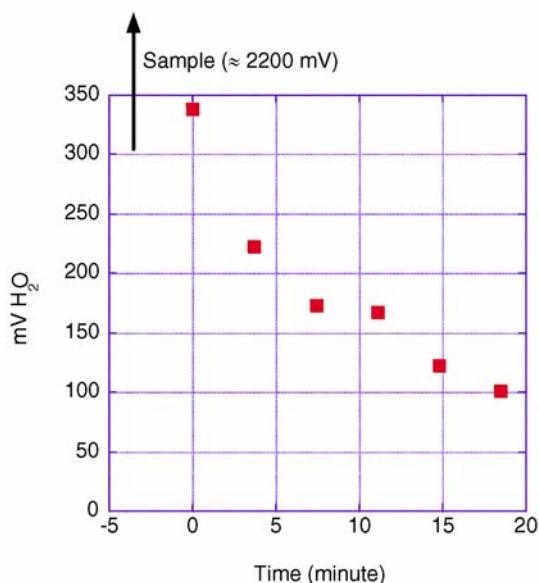
Fig. 3.2. Change in water vapor concentration (in millivolts) when a set of six (dry) standards are run, showing that some residual water vapor remains in the lines after water samples are equilibrated. (Water samples show an H_2O response of about 2200 mV.)

Table 3.2. Comparison of results of different water vapor correction routines

			$fCO_2(20)$		
Keyfield	**Lat. (N)**	**Pressure**	**Final**[a]	**Cruise**[b]	**New H$_2$0**[c]
45101	43	5239.7	762.9	765.80	745.8
45102	43	4994.3	765.7	768.80	748.5
45103	43	4499.7	769.5	771.45	751.7
45104	43	3983.9	768.5	770.30	751.8
45106	43	3001.5	758.4	760.50	742.1
45108	43	2000.5	755.2	756.60	738.6
45109	43	1800.0	761.4	762.90	745.3
45111	43	1401.5	746	747.80	729.8
45112	43	1200.0	728.4	730.10	712.9
45114	43	1001.0	724.1	725.70	708.1
45115	43	900.3	728.7	730.40	713.2
45116	43	800.7	712.4	714.00	696.6
45117	43	699.6	712.3	713.80	696.9
45118	43	601.3	687.2	689.00	672.7
45119	43	501.0	635.2	637.20	621.3
45121	43	401.1	576.8	578.60	563.8
45123	43	299.7	556.3	557.90	543.4
45125	43	201.0	510.7	512.10	499.1
45127	43	151.0	507.8	509.00	495.7
45129	43	99.7	494.1	495.30	482.3

Table 3.2 (continued)

Keyfield	Lat. (N)	Pressure	fCO$_2$(20)		
			Final[a]	Cruise[b]	New H$_2$0[c]
45130	43	79.6	486.6	487.80	474.8
45131	43	60.0	482.2	483.40	471.7
45132	43	39.5	450.7	451.80	440.2
45133	43	19.9	381.9	384.20	374.2
45135	43	3.4	374.7	375.30	365.6

[a] Final data reduction using the detector xCO$_2$ (dry) output.

[b] Data reduction on cruise using an empirical water vapor correction.

[c] Data reduction in Jan. 2004 using an empirical water vapor correction that was determined after the cruise.

correction algorithms. One empirical correction was established before the cruise, and one was determined from running wet versus dry standards after the cruise. The results show differences in the range from 7 to 17 µatm.

During the cruise a total of 1515 Niskin samples were analyzed for fCO$_2$, compared with 2500 TCO$_2$ samples. This was because only one full-time and a part-time operator were available for the work, while two full-time analysts were involved in TCO$_2$ analysis. A summary of the analysis statistics is given in Table 3.3.

The precision of the results is based on comparison of duplicate values and is estimated to be 2 µatm, or 0.3%. There is no apparent trend in imprecision with depth or absolute concentration when comparing absolute difference. The relative (percentage) difference is slightly higher for lower fCO$_2$ values found near the surface.

The A16N_2003a cruise overlapped or intersected with two previous cruises that were sampled by the AOML group.

Table 3.3. Analysis statistics for fCO$_2$(20)

Total number of stations	150
Total number of stations sampled for fCO$_2$ (full depth)	67
Total number of Niskin bottles tripped	4823
Total number of Niskin bottles sampled for fCO$_2$	1522
Number of duplicates	140
Number of bad values	6
Number of questionable values	48

The NAtl-93 cruise (Castle et al. 1998) followed the same track and was occupied during the summer of 1993 but the section was run from south to north. A 24-bottle rosette was used such that fewer depth samples were obtained and the spacing of the stations was nominal at 1°, compared to 0.5° spacing on the 2003 occupation.

The 24N-98 cruise was run in February 1998 and intersected the A16N-2003a section near 24°N, 26.5°W. In the comparison we make the assumption that changes in deep water are negligible over the time period. The crossover with the 24°N cruise is shown in Fig. 3.3. The fCO$_2$ shows a consistent offset, with the 2003 data being about 18 µatm higher than the 1998 data. For the comparison with the 1993 data we looked at the deep-water measurements for stations spaced about 5° apart (Fig. 3.4). Again, a systematic bias is observed, with the 2003 data being higher. The magnitude of the bias, however, is about 10 µatm. The cause of these disconcerting offsets is attributed to the water vapor correction. However, the exact reason or possible corrections is not readily apparent.

24N_1998, Station 26, Lat =24.5 N, Long = 26.4 W
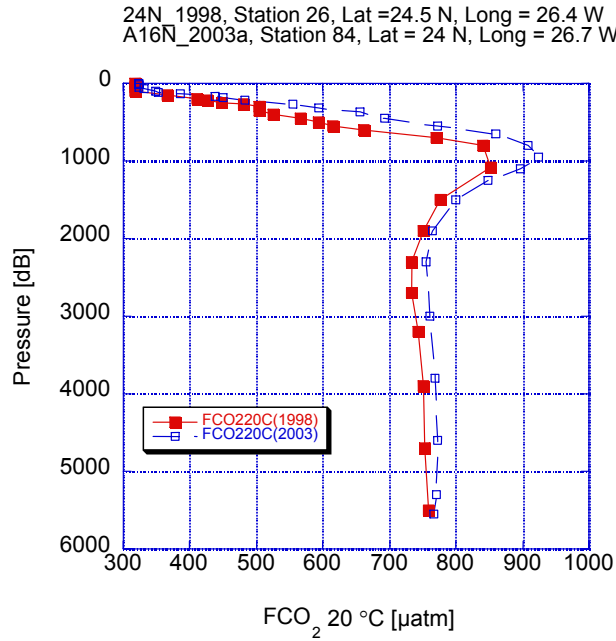A16N_2003a, Station 84, Lat = 24 N, Long = 26.7 W

Fig. 3.3. Comparison of *f*CO₂ (20) profiles for a crossover location between a cruise in 1998 and the A16N_203a cruise.
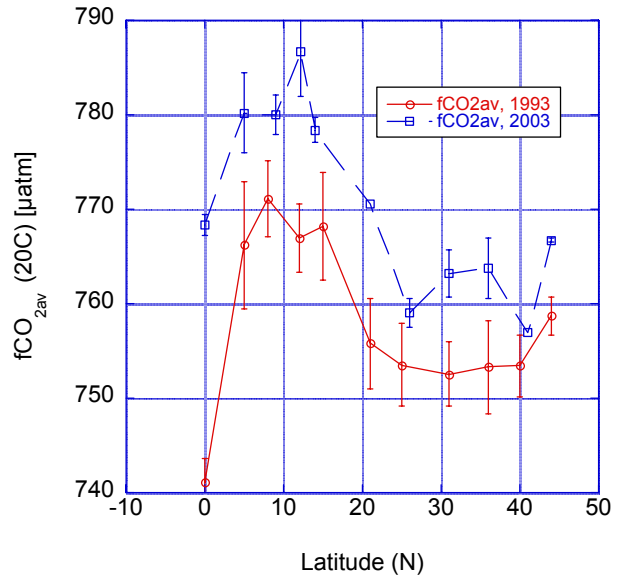
Fig. 3.4. Comparison of deep-water *f*CO₂ values for a cruise in 1993 and the A16N_2003a cruise at the depth range between 4000 and 5000 m.

The surface-water fCO₂ levels were measured with a different system in underway mode near sea surface temperature and offered an independent assessment of the agreement of fCO₂ values. However, the temperature correction has some uncertainties which complicate the comparison. For the comparison, the fCO₂(20) values were corrected to a sea-surface temperature (SST) as determined by the thermosalinograph using the empirical correction of $\partial fCO_2/\partial T = 0.0423°C^{-1}$ and by using the temperature dependence of the dissociation constant and using the thermodynamic equations of Mehrbach as refit by Dickson and Millero. The results, shown in Fig. 3.5 show the following average differences:

-3.30 ± 4.9 µatm (N = 76)) for fCO₂(UW) $- f$CO₂(disc)Mehr
-6.66 ± 4.1 µatm (N = 76) for fCO₂(UW) $- f$CO₂(disc)4.23%.

In the case of fCO₂(UW) $- f$CO₂(disc)Mehr, the fCO₂(20) are normalized to sea-surface temperature using the Mehrbach constants as refit by Dickson and Millero. For fCO₂(UW) $- f$CO₂(disc)4.23%, the fCO₂(20) are normalized to SST using the empirical relationship of $0.0423°C^{-1}$. Again, our temperature-corrected discrete data are on average higher than the underway measurements. The differences fCO₂(UW) $- f$CO₂(disc)Mehr and fCO₂(UW) $- f$CO₂(disc)4.23% are plotted against temperature in Fig. 3.6. There is a slight trend with temperature for the adjustments using the Mehrbach constants. Also, near 20°C, when the adjustment is small, the comparison shows that the discrete data is systematically higher. For the range from 18 to 22°C the difference is

-5.1 ± 4.9 µatm (N = 76) for fCO₂(UW) $- f$CO₂(disc)Mehr
-6.7 ± 4.1 µatm (N = 76) for fCO₂(UW) $- f$CO₂(disc)4.23% ,

very similar to the average difference over the entire temperature range, suggesting that the systematic offset is not attributable to the temperature correction alone.
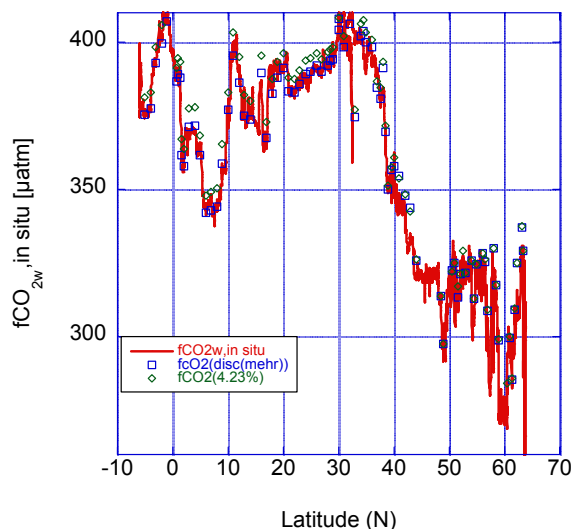
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Fig. 3.5. Comparison of underway fCO_2 measurements (line) with the discrete samples normalized to the same temperature as the underway measurements using an empirical relationship of 4.23% °C^{-1} (diamonds) and the constants of Mehrbach (open squares).
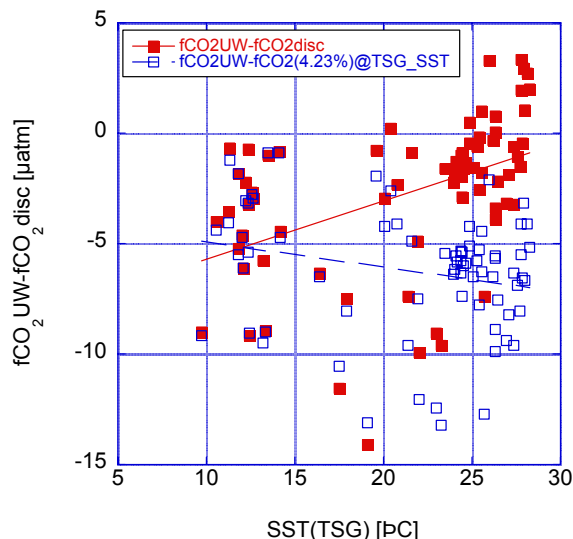
Fig. 3.6. Difference in underway fCO_2 measurements and with the discrete samples normalized to the same temperature as the underway measurements using an empirical relationship of 4.23% °C^{-1} (open squares) and the constants of Mehrbach (solid squares).

3.4 Total Alkalinity Measurements

Seawater samples for TALK were drawn from the Niskin bottles with a 40-cm length of silicon tubing. One end of the tubing was fit over the petcock of the Niskin bottle, and the other end was inserted into the bottom of a 500-mL Corning glass-stoppered sample bottle. The sample bottle was rinsed three times with approximately 300 mL of seawater. The sample bottle was slowly filled from the bottom. Once filled, the sample bottles were kept in a constant water bath at 25°C for a half-hour before analysis.

The titration system used to determine TALK consisted of a Metrohm 665 Dosimat titrator and an Orion 720A pH meter controlled by a personal computer (Millero et al. 1993). The acid titrant, in a water-jacketed burette, and the seawater sample, in a water-jacketed cell, were kept at 25 ± 0.1°C with a Neslab constant-temperature bath. The Plexiglas water-jacketed cells were similar to those used by Bradshaw and Brewer (1988), except that a larger volume (200 mL) was used to increase the precision. The cells had fill and drain valves with zero dead-volume to increase the reproducibility of the cell volume.

The HCl solutions used throughout the cruise were made, standardized, and stored in 500-mL glass bottles in the laboratory for use at sea. The 0.23202 M HCl solutions were made from 1 M Mallinckrodt standard solutions in 0.45 M NaCl to yield an ionic strength equivalent to that of average seawater (≈0.7 M). The acid was standardized using a coulometric technique by the University of Miami and by Dr. Dickson of SIO. The two standardization techniques agreed to ±0.0001 N.

The volume of HCl delivered to the cell is traditionally assumed to have a small uncertainty (Dickson 1981) and is equated with the digital output of the titrator. Calibrations of the Dosimat burettes with Milli Q water at 25°C indicated that the systems deliver 3.000 mL (the value for a titration of seawater) to a precision of 0.0004 mL. This uncertainty resulted in an error of 0.4 µmol/kg in TALK.

The titrators were calibrated in the laboratory before the cruise. CRM Batch 59, prepared by Dr. Dickson, was used at sea to monitor the performance of the titrators. All TALK data have been corrected based on CRM values for each cell and each leg (Millero et al. 2000); see Table 3.4.

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Table 3.4. Total alkalinity certified reference material measurements (TCO$_2$ and pH values calculated from TALK titrations)

	TALK (µmol/kg)	TCO$_2$ (µmol/kg)	pH (total scale) @ 25°C	Total no. of runs
Leg 1				
System 1	2222.2 ± 3.6	2015.0 ± 3.7	7.891 ± 0.007	15
System 2	2224.2 ± 3.2	2017.7 ± 3.4	7.893 ± 0.007	17
Leg 2				
System 1	2222.5 ± 4.5	2012.1 ± 2.4	7.895 ± 0.009	16
System 2	2222.9 ± 3.8	2016.1 ± 4.1	7.890 ± 0.009	15
Manual system	2217.2 ± 2.1	2013.4 ± 0.5	7.888 ± 0.006	3
Both Legs				
System 1	2222.4 ± 3.8	2013.6 ± 3.4	7.891 ± 0.011	33
System 2	2223.6 ± 3.5	2017.0 ± 3.8	7.891 ± 0.008	30
Manual system	2217.2 ± 2.1	2013.4 ± 0.5	7.888 ± 0.006	3
All systems	2222.7 ± 3.6	2015.2 ± 3.5	7.891 ± 0.009	66
Certified Values				
CRM Batch 59	2220.98	2007.1	7.895a	
			7.9674 ± 0.0005b	19
TRIS			8.0855 ± 0.0003a	19
Correction Factor, Leg 1				
System 1	0.9994	0.9961	0.004	
System 2	0.9980	0.9947	0.002	
Correction Factor, Leg 2				
System 1	0.9988	0.9975	0.000	
System 2	0.9991	0.9958	0.005	
Manual system	1.0017	0.9969	0.007	

3.5 pH Measurements

Seawater samples were drawn from the Niskin bottles with a 20-cm length of silicon tubing. One end of the tubing was fit over the petcock of the Niskin bottle, and the other end was attached over the opening of a 10-cm glass spectrophotometric cell. The spectrophotometric cell was rinsed three to four times with a total volume of approximately 200 mL of seawater; the Teflon endcaps were also rinsed and then used to seal a sample of seawater in the glass cell. While drawing the sample, care was taken to make sure that no air bubbles were trapped within the cell. The sample cells were kept in a water bath at 20°C for a half an hour before analysis.

Seawater pH was measured using the spectrophotometric procedure (Byrne 1987) and the indicator calibration of Clayton and Byrne (1993). The indicator was an 8.0-mM solution of m-cresol purple sodium salt (C$_{21}$H$_{17}$O$_5$Na) in MilliQ water.

The absorbance measurements were made using a Varian Cary 2200 spectrophotometer. The temperature was controlled to a constant temperature of 25°C with an Endocal RTE 8DD refrigerated circulating temperature bath that regulates the temperature to ± 0.01°C. The temperature was measured using a Guildline 9540 digital platinum resistance thermometer.

4. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-085) is available free of charge from CDIAC. The complete documentation and data can be obtained from the CDIAC oceanographic web site (http://cdiac.ornl.gov/oceans/doc.html), through CDIAC's online ordering system (http://cdiac.ornl.gov/pns/how_order.html), or by contacting CDIAC.

The data are also available from CDIAC's anonymous file transfer protocol (FTP) area via the Internet. (Please note that your computer needs to have FTP software loaded on it. It is built in to most newer operating systems.) Use the following commands to obtain the database:

```
ftp cdiac.ornl.gov or >ftp 160.91.18.18
Login: "anonymous" or "ftp"
Password: your e-mail address
ftp> cd pub/ndp086/
ftp> dir
ftp> mget (files)
ftp> quit
```

The full datasets from the cruise, including bottle and CTD data, can be found at the CLIVAR repeat hydrography website: http://ushydro.ucsd.edu/cruise_data_links.html

Contact information:

Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, Tennessee 37831-6335
USA

Telephone: (865) 574-3645
Telefax: (865) 574-2232

E-mail: cdiac@ornl.gov
Internet: http://cdiac.ornl.gov/

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