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CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA FROM THE F/S METEOR CRUISE NO. 18 IN THE NORTH ATLANTIC OCEAN (WOCE SECTION A1/E) DURING SEPTEMBER 1991

Contributed by
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ABSTRACT

Johnson, K. M. [1], B. Schneider [2], L. Mintrop [3], D.W. R. Wallace [1]. 1995. Carbon Dioxide, Hydrographic, and Chemical Data From the F / S Meteor Cruise No. 18 in the North Atlantic Ocean (WOCE Section A1 / E) During September 1991.

Herein are given the procedures and methods used to obtain total carbon dioxide (C_T), total alkalinity, and underway pCO_2 data during the F / S Meteor Cruise 18 in the North Atlantic Ocean (WOCE Section A1 / E). Instructions for accessing the data are provided.

The F / S Meteor departed Reykjavik on September 2, 1991 and docked in Hamburg early on the morning of September 25, 1991 after 24 days at sea. A two day steam from Reykjavik brought the ship to the starting position for WOCE zonal section A1 / east (A1 / E) on September 5. Section work began and ended with a closely spaced series hydrocasts on the SE-Greenland (60 °N 42 ° 30' W) and Porcupine Shelves (52 ° 20' N 14 ° 15' W), respectively. The cast schedule was interrupted for equipment problems (6 and 7 September), current meter deployments (9,10, 11, 14, and 19 September), and by high seas (13, 14, and 17 September). Of 64 CTD casts made, 58 were bottle casts including two calibration stations. Measurements made included CTD pressure, temperature, salinity, bottle salinity, oxygen, phosphate, nitrate, nitrite, silicate, total alkalinity, CFC's, total carbon dioxide, and continuous underway pCO_2 of surface waters. Carbonate samples were collected from 31 section stations (55.4 % of the section stations), one test station, and two calibration stations. Repeated XBT, and ADCP profiles were taken throughout the cruise.

The C_T was measured using an automated sample processor (SOMMA) for extracting CO_2 from seawater samples coupled to a Coulometer for detection of the extracted CO_2. The precision and accuracy of the system was ± 1.60 μmol / kg. Samples collected for total alkalinity were measured using standard potentiometric techniques; precision was ± 2.0 μmol / kg. Underway pCO_2 was measured by Infra Red (IR) Photometry; precision was ± 2 μatm. The work aboard the F / S Meteor was supported by the U. S. Department of Energy under contract DE-ACO2-76CH00016, and the Bundesministerium fuer Forschung und Technologie (BMFT) through grants 03F0545 A and MFG 099 / 1.

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1. BACKGROUND INFORMATION

The World Ocean Circulation Experiment - World Hydrographic Program (WOCE - WHP) is a major component of the World Climate Research Program whose overall goal is to better understand the ocean's role in climate and climatic changes resulting from both natural and anthropogenic causes. Although total carbon dioxide (C_T) is not an official WOCE measurement, a coordinated effort, supported in the USA by the Department of Energy (DOE), is being made on WOCE cruises through 1998 to measure the global spatial and temporal distributions of C_T and other parameters in order to estimate the meridional transport of inorganic carbon in a manner analogous to the oceanic heat transport (Bryden and Hall, 1980; Brewer et al., 1989; Roemmich and Wunsch, 1985), and to build a data base suitable for carbon-cycle modeling and the subsequent estimation of anthropogenic CO_2 increase in the oceans. The CO_2 Survey is taking advantage of the sampling opportunities provided by the WOCE-WHP Cruises during this period. The final data set is expected to cover on the order of 23,000 stations.

This cruise, Meteor 18, from Reykjavik, Iceland to Hamburg, Germany from 2 - 25 September 1991 completed WOCE zonal Section A1/E. It was also one of a series of cruises starting in 1991 belonging to the North Atlantic Overturning Rate Determination (WOCE-NORD) program coordinated jointly between the Bundesamt fuer Seeschiffahrt und Hydrographie, Hamburg and the Institut fuer Meereskunde, Hamburg involving seasonally repeated Hydrographic sections between southern Greenland and Iceland in combination with current measurements from moored arrays. Program objectives include the direct determination of the overturning rates and the intensity of the meridional transports of mass, heat, and salt. The A1/E section was chosen to be south of the major wintertime convection regions to avoid water mass formation processes while at the same time avoiding shallow topography which could cause difficulties in calculating volume transports.

This document describes the cooperative effort of chemical oceanographers from Brookhaven National Laboratory and the Institut fuer Meereskunde Kiel (IFMK) to make high quality CO_2 measurements on WOCE Section A1/E during a 24 day expedition in the North Atlantic Ocean aboard the F / S Meteor in September 1991.

2. DESCRIPTION OF THE EXPEDITION

2.1 R/V Meteor

The Forschungs Schiff (F / S) Meteor is owned by the Federal Republic of Germany through the Ministry of Research and Technology (BMFT) who also financed its construction. It is operated by the German Research Foundation (DFG) who provide about 70 % of its operating funds with the remainder coming from the BMFT. The DFG also plans the scientific cruises and appoints the Chief Scientists. The Operations Control Office of the University of Hamburg is responsible for the management, logistics, and the execution and supervision of ship operations. These functions are exercised through direct cooperation with expedition coordinators and through the managing owners, the Reedereigemeinschaft Forschungsschiffahrt (RF) GmbH, located in Bremen, Germany. The latter is responsible for hiring, provisioning, and coordinating ship maintenance. The Meteor is used for ocean research primarily in the Atlantic and Indian Oceans, and routinely carries scientists from many different countries. The Meteor was completed in 1986 in Travemunde, Germany:

Port of Registration	Hamburg
Call Sign	DBBH
Displacement	4780t
Length	97.5 m
Beam	16.5 m
Draught (maximum)	5.6 m
Speed	12 kn
Depth Main Deck	7.7 m
Personnel	Crew: 32; Scientists: 30
Main Engine	4 x Mak6M 322 = 4 x 1000 kW at 750 rpm
Maximum Cruise Duration	60 days
Science Quarters	20 laboratories on main deck (approx. 400 m^2)

2.2 R / V Meteor Cruise No. 18 Information

Ship Name	Meteor
Cruise / Leg	Cruise No. 18
Location	Reykjavik, Iceland to Hamburg, Germany
Dates	September 2 - September 25, 1991
Funding	Deutsche Forschungs Gemeinshaft (DFG) U. S. Department of Energy (DOE)
Chief Scientist	Professor Dr. Jens Meincke
Master	Heinrich Bruns

Parameters measured, institution, and responsible Investigators

Parameter	Institution	PI
CTD, Salinity, XBT	BSH	A. Sy
Nutrients	SIO-ODF	J. Swift, D. Bos, D. Muus
Oxygen	SIO-ODF	J. Swift, D. Bos, D. Muus
CFM's	UBP	W. Roether, A. Putzka
Tritium, He, ^{14}C	IUPH	R. Bayer
C_T	BNL, IFMK	K. Johnson, B. Schneider, A. Morak, R. Ramirez
pCO_2	IFMK	B. Schneider
Alkalinity	IFMK	L. Mintrop, A. Korves
ADCP	IFMH	M. Bersch, J. Meincke
Rain Gauges	IFMK	H.-J. Isemer

Participating Institutions

BNL	Brookhaven National Laboratory
BSH	Bundesamt für Seeschiffahrt und Hydrographie
IFMH	Institut fuer Meereskunde der Universität Hamburg
IFMK	Institut fuer Meereskunde der Universität Kiel
IUP	Institut für Umweltphysik der Universität Heidelberg
SIO-ODF	Scripps Institution of Oceanography - Ocean Data Facility
UBP	Universität Bremen, Fachbereich Physik
OSU	Oregon State University

2.3 Brief Cruise Summary

The BNL CO_2 group consisting of K. M. Johnson and R. Ramirez arrived in Reykjavik on August 29, and went aboard the next day to join the Kiel CO_2 group under the direction of Drs. Bernd Schneider, and Lutger Mintrop. Dr. Jens Meincke was already aboard as Chief Scientist. Setting up of the equipment began on the 30th, and was completed on the morning of September 2. The F / S Meteor departed Reykjavik at 11 am on September 2, 1991 under captain Heinrich Bruns. We immediately encountered rough weather conditions with gale force winds of Beaufort 8 - 9. Two test stations were taken during the transit across the Denmark Straight to the first WOCE station (no. 558) on the SE-Greenland shelf on September 5 . The earlier gale force winds were replaced by a quiet period characterized by humid air masses over cold water resulting in fog. The hydrocast routine was interrupted by winch and / or rosette bottle release problems on September 6 and 7, and current meter deployments on September 9, 10 ,11, 14, and 19 September. Bad weather forced several delays when a low passed just north of the Meteor to drop the pressure to 980 hPa causing a work pause on September 13 when winds gusted up to 11 Beaufort and the seas rose to 8 m. This scenario was repeated on September 17, and the slowly receding sea states thereafter, continued to plague the oceanographic work until the end of the Hydrographic program with station 622 on September 21. Each especially rough period was followed by reduced sampling stations (12 instead of 24 bottles on each rosette), but these stations were restricted to short lines perpendicular to the WOCE line. The station locations are shown in Figure 1. Only station 607 of the 6 stations (592, 593, 595, 606, 607, and 608) taken normal to the WOCE line was sampled for carbonate system parameters. XBT measurements were made at selected CTD stations in parallel with the CTD casts, and acoustic Doppler current profiles (ADCP) to measure the instantaneous near surface currents were made continuously from September 2 to September 22. The distribution of the recording current meter moorings (A-F) to measure the long-term currents along the A1 / E section is shown in Figure 2.

There were two Single-Operator Multiparameter Metabolic Analyzers (SOMMA) from BNL (hereafter BNL I and BNL II) on board for this cruise, one potentiometric alkalinity titrator from IFMK, and an IR-based system for underway pCO_2 belonging to IFMK. Not counting duplicates, 583 total carbonate samples, normally in conjunction with tracer samples, were taken from 31 section stations, one test station (557) and two calibration stations (581, 608) out of a total of 58 bottle casts. All 58 stations could not be sampled for tracers and C_T because of the time required for analysis. The standard WOCE parameters (oxygen, nutrients, and salinity) were sampled on all stations, and on approximately every other station these were augmented by the tracer samples for CFC, carbonate, helium, tritium, and radiocarbon as the ship steamed eastward from the southeastern tip of Greenland to the Irish Coast. Thus the density of the CO_2 sampling was fairly constant at approximately 2 stations per day, while the underway pCO_2 system operated continuously.

Both electrical and mechanical problems were noted for each of the SOMMA-Coulometer Systems. BNL II was most severely affected. It was declared nonoperational on September 16 when the magnetic valves on the SOMMA chassis could no longer be operated reliably, the electronic calibration factor suddenly changed by + 0.11 % (a factor of 10 higher than the usual precision of ± 0.01 %), and the communication between the keyboard and PC became erratic. The final Certified Reference Material (CRM) run on this date was 6 µmols / kg lower than the certified value, and test sample duplication was equally poor. When this system was operated several months later in the laboratory all components functioned satisfactorily so we were unable to determine the cause of the shipboard difficulties. BNL I experienced two serious problems. The BNL I Coulometer was lost when the photodetector amplifier failed on September 7. Fortunately, a back-up Coulometer from Kiel was available, and it was immediately placed in service. Secondly, the gas calibration system apparently failed on September 10 due to cross-talk between the the gas sample loops (CO_2 leaking from one loop into the other via a surface scratch or scoring of the valve which contaminated the carrier gas). This manifested itself as a very noisy system with a very high and unusable blank. It was corrected by disconnecting the gas sample valve from the system so that the carrier gas (N_2) passed directly from the gas cylinder into the SOMMA stripper.

Due to the rough weather, plans for a return voyage around the north of Scotland to Hamburg were changed, and the ship arrived in Hamburg on September 25, via the English Channel where winds astern arising from a low pressure near the Faeroe Islands hastened the return voyage.

3. DESCRIPTION OF METHODS

Water samples were collected in 24 General Oceanics 10 l-Niskin bottles mounted on a Neil Brown Mark III instrument (S/N NB3) provided by the Institut fuer Meereskunde Kiel (IFMK). Data was acquired at a rate of 32 ms / cycle using Oceansoft rev. 3.1 (EG & G). Further details are given by Meincke (1993), and additional data concerning post and precruise laboratory calibrations of the CTD temperature, pressure, conductivity, and oxygen sensors may be found in Siedler and Zenk (1992), and the WHP One-Time Section A9 Data Report (1994). ADCP measurements to a depth of 300 m were made nearly continuously (some breaks for rough weather and minor computer malfunctions) from September 2 - 22 with a hull-mounted system from RD Instruments (San Diego) using a pulse frequency of 150 KHz.

The rosette systems used with the CTD on this cruise were subject to various mechanical / electrical problems such that tripping failures were not uncommon--especially at stations 596 - 613. Repeated checks on board and several careful verifications using the complete bottle data sets have been carried out, and the current pressures for each sample are considered correct by the responsible personnel. Reversing thermometers of both the electronic (SIS, Kiel) and mechanical (Gohla Precision, Kiel) types were also read at the completion of each cast. In so far as possible, the processing and quality control of CTD and bottle data done at BSH followed the published guidelines in the WOCE Operations Manual (WHPO 91-1, 1991). **Salinity** corrections were made using bottle salinities measured 1 - 2 days after collection and determined on a Guildline Autosal model 8400A standardized at each station with IAPSO water (batch P112). Due to temporal conductivity sensor shifts, the corrections were made for station nos. 558 - 566, 567 - 602, and 603 - 622 separately. The final salinity data is expected to be accurate to ± 0.002 PSU. **Oxygen** sensor data correction was carried out according to the guidelines given by Millard (1991). Bottle **oxygen** was determined by Winkler titration after the technique of Carpenter (1965) with the modifications of Culberson et al. (1991) using standards and blanks run in seawater. Subsequently, all Winkler results were recalculated and verified by ODF in La Jolla. The concentrations of **nitrate**, **nitrite**, **phosphate**, and **silicate** dissolved in seawater were determined on samples collected in high density polyethylene screwcapped bottles using a Technicon Autoanalyzer according to procedures given in Hager et al. (1972) and Atlas et al. (1971), using the spectrophotometric methods of Armstrong et al. (1967) and Bernhardt and Wilhelms (1967). The analyses were completed within 24 hours of sampling including storage at 6 °C for no more than 15 hours. Preweighed standards were used to prepare the working standard on board ship.

The total **carbon dioxide concentration** (C_T) was determined using an automated coulometric system (SOMMA) described and designed by K. M. Johnson and co-workers (Johnson et al., 1985; Johnson et al., 1987, Johnson and Wallace, 1992). Some 583 individual samples along with 158 duplicates (total analyzed = 741) from 33 stations were collected in 300 mL precombusted (450 °C for 24 h) BOD bottles and immediately poisoned with $HgCl_2$ according to the DOE Handbook of Methods (DOE, 1994). Before analysis, they were kept in darkness in a cold room until thermally equilibrated to the analytical temperature. Some 61 Certified Reference Materials (CRM) supplied by Dr. Andrew Dickson of the Scripps Institution of Oceanography (see DOE Handbook of Methods, 1994) were also analyzed (37 on BNL I and 24 on BNL II). The CRM were from Batch 7 which was a filtered sterile salt solution (S = 37.12) spiked with Na_2CO_3 analyzed for C_T by vacuum - extraction / Manometry in the laboratory of C. D. Keeling at SIO. The certified C_T value was 1926.39 ± 0.91 μmol / kg (n = 13).

Seawater introduced from an automated To Deliver (TD) pipette into a stripping chamber was acidified and the resultant CO_2, after drying, was coulometrically titrated on a model 5011 UIC Coulometer. In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO_2 and ethanolamine was titrated coulometrically (electrolytic generation of OH^-) with photometric endpoint detection. The product of the current passed through the cell during the titration and time was related by Faraday's Constant to the number of moles of OH^- generated and thus to the moles of CO_2 which reacted with ethanolamine to form the acid. The SOMMA-Coulometer System was calibrated with pure CO_2 using hardware consisting of an 8 port Gas Sampling Valve (GSV) with two sample loops connected to a source of pure CO_2 through an isolation valve with the vent side of the GSV plumbed to a barometer. When a gas loop was filled with CO_2, the mass (moles) of CO_2 contained therein was calculated by multiplying the loop volume (V) by the density of CO_2 at the ambient T and P. Density was calculated from the molar volume of CO_2 ($V(CO_2)$) obtained iteratively from an equation of state using the instantaneous barometric pressure (P), loop temperature (T), and the first virial coefficient $B(T)$ for pure CO_2:

$$V(CO_2) = RT / P \ (1 + B(T) / V(CO_2))$$

The ratio of the calculated mass to that determined coulometrically, was the gas calibration factor (CALFAC) used to correct the subsequent titrations for small departures from 100 % theoretical (see DOE Handbook of Methods, 1994). The volume of the loops was determined gravimetrically with deionized water by the method of Wilke et al. (1993). The standard operating procedure was to make gas calibrations daily, or for each new titration cell used (normally, one cell per day).

The " to deliver " volume (TDV) of the SOMMA sample pipette was determined before the cruise gravimetrically with milli-Q deionized water which had been degassed with Helium. The thermostatted sample pipette was filled with water at the same temperature, and then discharged into preweighed 50 mL serum bottles which were reweighed on a model R300S (Sartorius, Göttingen, Germany) balance. The apparent weight (g) of water collected (W_{air}) was corrected to the mass in vacuo (M_{vac}) from:

$$M_{vac} = W_{air} + W_{air}(.0012 / d - .0012 / 8.0)$$

where .0012 is the sea level density of air at 1 atm, *d* is the density of the calibration fluid at the pipette temperature and sample salinity, and 8.0 is the density of the stainless steel weights. The to deliver volume (TDV) was:

$$TDV = M_{vac} / d.$$

This procedure was repeated at sea except the serum bottles were crimp-sealed and reweighed on shore within three weeks of collection. The precruise calibrated " to deliver " volume of the pipette for system BNL I was 28.7108 mL at 20 °C. During the cruise the pipette temperature was kept at approximately 10.2 ± 0.3 °C. The calculated TDV at 10.2 °C (TDV_{T2}) was 28.7080 mL from:

$$TDV_{T2} = TDV_{T1} [1 + a_v (T_2 - T_1)]$$

where a_v is the coefficient of volumetric expansion for pyrex-type glass (1×10^{-5} °C^{-1}), T_2 the measurement temperature, and T_1 the calibration temperature. The corresponding results for the BNL II pipette were 29.6954 and 29.6925 mL, respectively. During the cruise 8 TDV samples were collected at 10.2 °C from the BNL I pipette and sealed for reweighing. The TDV from these weighings was 28.6845 ± 0.0058 mL (0.02 %) which differed from the calculated TDV of 28.7080 mL by - 0.0235 mL or - 0.082 %. For the BNL II pipette 11 samples were taken at 10.2 °C which gave a TDV of he 29.6712 ± 0.0065 mL (0.02 %) which differed from the calculated TDV of 29.6925 mL by - 0.0213 mL or - 0.072 %. Because the original laboratory calibration took place at 20 °C, while all of the analytical work aboard ship was done at 10.2 ± 0.3 we have used the latter (shipboard) results for TDV to calculate the C_T values (i.e., for BNL I, TDV = 28.6845 mL; for BNL II, TDV = 29.6712 mL). Interestingly, the data confirmed our current practice of ensuring identical calibration and analytical temperatures because it appeared that just correcting for glass expansion was not adequate to describe the TDV at temperatures significantly different from the calibration temperature (see also DOE (1994)).

An IBM compatible computer with two RS232 serial, a 24 line Digital Input / Output (I / O), and Analog to Digital (A / D) ports was used to control the coulometer, barometer, solid state control relays, and temperature sensors, respectively. The temperature sensors (model LM34CH, National Semiconductor, Santa Clara, CA) with a voltage output of 10 mV / °F built into the SOMMA were calibrated against thermistors certified to 0.01 °C (PN CSP60BT103M, Thermometrics, Edison, NJ) using a certified mercury thermometer as a secondary standard. These sensors monitored the pipette, gas sample loop, and the coulometer cell temperatures. The barometer, model 216B-101 Digiquartz Transducer (Paroscientific, Inc. Redmond, WA) was factory-calibrated for pressures between 11.5 and 16.0 psia. The SOMMA software was written in GWBASIC Version 3.20 (Microsoft Corp., Redmond, WA), and the instrument was driven from an options menu appearing on the PC monitor.

The analytical method for C_T used for Cruise No. 18 differed from the technique described in an earlier data report (Johnson et al., 1995) for Meteor Cruise No. 15 (March 1991) in that an electronic calibration procedure was used to check the theoretical response of the coulometers's voltage to frequency converter (VFC) as described in Johnson et al. (1993) and DOE (1994). Briefly, at least two levels of current (usually 50 and 2 mA) were passed through an independent and very precisely known resistance (R) for a known time. The voltage (V) across the resistance was continuously measured and the instantaneous current (I) across the resistance was calculated from Ohm's law and integrated over the calibration time. Then the number of pulses (counts) accumulated by the VFC during this time was compared to the theoretical number computed from the factory-calibration of the VFC (frequency = 10^5 pulses (counts) generated / sec at 200 mA) and the measured current. If the VFC was perfectly calibrated, electronic calibration yielded a straight line passing through the origin (intercept = 0) with a slope of 1. Calibrations and titrations were done with the coulometer in the counts mode (the total charge passed during a titration was displayed as the number of counts accumulated by theVFC). From the factory-calibration of the VFC, and the value of the Faraday (96489 Coulomb / mol) a scaling factor of 4.82445×10^3 counts / µmol was derived, and the theoretical number micromoles of Carbon titrated (m) was:

$$m = [\text{Counts} / 4824.45 - (\text{Blank} * T_T) - (\text{ECint} * I_T)] / \text{ECslope}$$

where T_T was the length of the titration in minutes, Blank the system blank in µmol / min, ECint was the intercept from electronic calibration in µmol / min, I_T the time of continuous current flow in min, and ECslope was the slope from electronic calibration. Note that the slope obtained from the electronic calibration procedure applied for the entire length of the titration, but the intercept applied only for the period of continuous current flow (usually 3 - 4 min). The sample total carbon dioxide concentration (C_T) in µmol / kg was calculated from:

$$C_T = [\, m * (\mathrm{CALFAC}) * (1000 / \mathrm{TDV}_T * p\,)] * 1.00017$$

where CALFAC is the gas calibration factor, TDV_T is the " to deliver " volume of the pipette in mL at the analytical temperature, p is the density of sea water in kg / L from the equation of state (Millero and Poisson, 1981), and 1.00017 corrects for the dilution of the sample by the 100 µL of $HgCl_2$ solution added to the sample bottle.

As a consequence of the coulometer and gas calibration problems described in section 2.3, BNL I was operated after September 12 without a functioning gas calibration system. For sample C_T calculations after September 12, the mean calibration factor (CALFAC) of 1.002844 (n = 7) obtained for the period 4 thru 10 September was used between September 13 and September 23. No samples were run on BNL I on September 11 and 12. System BNL II was continuously operated between September 4 and 15 and calculations were made using the daily gas calibration factors for that instrument. No samples were run on system BNL II after 15 September. The results of the CRM analyses are shown in Table 1.

Table 1. Accuracy: Summary of CRM C_T analyses made aboard the F / S Meteor during Cruise no. 18 in September 1991 with two SOMMA-Coulometer Systems (BNL I and BNL II). The CRM were from batch 7 and had a salinity of 37.12 and a C_T of 1926.39 ± 0.91 µmol / kg (n=13).

System	No. (n)	Mean µmol / kg	S. D. µmol / kg	R. S. D. %	Difference found - CRM	Period
BNL I[a]	14	1926.19	0.89	0.05	- 0.20	4 - 10 September
BNL I[b]	23	1925.66	1.46	0.08	- 0.73	13 - 23 September
BNL II	24	1926.90	1.65	0.09	+ 0.51	4 - 15 September
Combined	61	1926.27	1.52	0.08	- 0.12	4 - 23 September

[a] Period with functioning gas calibration unit (September 4 - 10).

[b] Period without a functioning gas calibration unit (September 13 - 22).

This was the first cruise where two complete SOMMA systems were employed side-by-side to analyze samples from the same profile, and in addition to the CRM analyses, measurements of system precision and bias were made. The system precision data are given in Table 2. For these data, "within-sample" precision was the average difference between two replicates analyzed from the same BOD bottle, "between-sample" precision was the average difference between duplicate samples taken from a single Niskin Bottle, "between-Niskin" precision was the average difference between single bottles taken from two Niskin Bottles closed at the same depth, and Sp^2 was the pooled standard deviation from the combined analyses of samples filled from multiple Niskin Bottles closed at the same depth (stations 557, 581, and 608) and analyzed over a period of several days. The Sp^2 was the square root of the the pooled variance according to Youden (1951):

$$S_p{}^2 = \frac{\sum_{i=1}^{K}\left(\sum_{j=1}^{n_i}(x_{ij}-\bar{x}_j)^2\left[\left(\sum_{j=1}^{n_i}(x_{ij}-\bar{x}_j)^2\right/ n_i\right]\right)}{\sum_{i=1}^{K} n_i - K}$$

Table 2. Precision: Summary of sample precision for C_T analyses made aboard the F / S Meteor during Cruise no. 18 in September 1991 with two SOMMA-Coulometer Systems (BNL I and BNL II). Precision data, except for Sp^2, are given as the absolute value of the average differences [a] between duplicates. The number of comparisons (n) are shown in parentheses, while for Sp^2, k is the number of test sample station data sets from each instrument and n is the combined number of samples analyzed by both instruments.

System	Bottle Precision (± µmol / kg)			Sp^2
	within-sample (n)	between-sample (n)	between-Niskin (n)	(k,n)
BNL I	0.77 (18)	0.73 (31)	0.39 (12)	1.49 (3,26)
BNL II	1.10 (19)	0.83 (3)	0.65 (3)	1.68 (2,26)
Totals	0.93 (37)	0.79 (34)	0.52 (15)	1.59 (5,52)

[a] $\sum_{x=1}^{n} \text{abs} (x_1 - x_2) / n$ where n is the number of comparisons between duplicates x_1 and x_2.

The combined precision (Sp^2) for the A1 / E samples was ± 1.59 µmol / kg which agreed very well with the precision of the CRM analyses (± 1.52 µmol / kg, n = 61, Table 1). Note that BNL I, as a rule, gave slightly better precision than BNL II, and that the other precision estimates were consistently better than Sp^2, however, the higher figure of ± 1.59 µmol / kg was considered to be the appropriate estimate of overall analytical precision because it included all sources of error--instrumental, calibration, and sampling--encountered over a period of several days.

System bias was checked by analyzing the calibration station (581) samples from a depth of approximately 2033 m on both instruments over several days. For BNL I the mean result was 2159.07 ± 0.61 µmol / kg (n =5, analyzed between September 12 and 16), and the corresponding result for BNL II was 2158.26 ± 1.18 (n = 12, analyzed between September 11 and 13). The absolute value of the difference was 0.81 µmol / kg with BNL I giving a slightly higher result. In addition, duplicate bottles from 33 samples were analyzed on each instrument during the period 4 to 15 September. The bias data are summarized in Table 3.

Table 3. Bias: Summary of sample C_T analyses for duplicate samples where one of the duplicates was analyzed on SOMMA-Coulometer System BNL I, and the other was analyzed on System BNL II aboard the F / S Meteor during Cruise No. 18. Only the analyses made between September 4 - 15, 1991, when both instruments were operational are included in this table.

Comparison	BNL I (n)	BNL II (n)	Difference (I - II)	Abs (I - II)
CRM	1926.32 (19)	1926.90 (24)	- 0.58	0.58
Station 581	2159.07 (5)	2158.26 (12)	+ 0.81	0.81
All Stations	2125.75 (33)	2127.48 (33)	- 1.73	1.87
Means			- 0.50	1.09

In aggregate, Tables 1 - 3 indicated that while System BNL I tended to give slightly lower results, any instrumental bias was within the overall precision found for the entire data set (± 1.59 µmol / kg, Table 2), and accordingly no correction of any kind for instrumental bias has been applied to the data.

As a final estimate of data quality, duplicate samples from 7 Niskin bottles at five stations were collected for later shore-based reference analyses of C_T in the laboratory of Dr. Charles Keeling at SIO by vacuum extraction / Manometry. The results are given in Table 4 where the BNL data are compared to the SIO results (Guenther et al., 1994). Temperature sensors were not included in the shipping crates, as is now standard operating procedure, so the temperature history of these samples was not known between cold storage aboard ship and their arrival at SIO.

Table 4. Comparison of shipboard analyses of C_T by Coulometry (BNL) during the M 18 Cruise, and the shore-based reference analyses of C_T by Manometry on duplicate samples in the laboratory of C. D. Keeling at the Scripps Institution of Oceanography (SIO). The reference analyses were made in February - March 1994. This table supersedes Tables 3e and 5e of Guenther et al. (1994). Abbreviations: sample, Spl; salinity, S.

Station	Spl Date	Niskin	Depth (m)	C_T (BNL) µmol / kg	C_T (SIO) µmol / kg	Diff. BNL - SIO	S Diff.[a]
575	09.09.91	24	10	2088.25	2087.98	+ 0.27	+ 0.002
575	09.09.91	13	1095	2152.24	2154.55	- 2.31	- 0.019
580	10.09.91	23	27	2085.75	2094.58	- 8.83	- 0.003
580	10.09.91	1	2367	2157.52	2160.00	- 2.48	- 0.003
581[b]	10.09.91	2	2033	2158.48	2158.73	- 0.25	- 0.004
596	14.09.91	14	690	2167.83	2167.74	+ 0.09	- 0.005
603	16.09.91	1	4063	2202.42	2203.84	- 1.42	- 0.001
means						- 2.13	- 0.005

[a] The difference between the ship's CTD sample salinity and the salinity measured at SIO.

[b] The calibration station. The BNL result is the mean of 17 analyses on the two systems between 11 and 16 September.

Note that our final C_T data (Table 4) differ from the preliminary C_T results furnished by us to SIO and reproduced in Guenther et al. (1994). Table 4 of this report therefore supersedes Tables 3e and 5e of Guenther et al. (1994), and should be referenced for the M18 (A1 / E) C_T data in all future work. Six of the seven differences were within the analytical precision of the methods, and salinities agreed to within 0.005 ruling out evaporative losses giving additional weight to these data and the data set as a whole. Figure 3 is a color section plot of the WOCE-WHP A1 / E section.

Alkalinity (A_T) samples were collected in 500 mL bottles with the same precautions as for total carbon dioxide. They were stored in the dark at 4 °C and analyzed within 24 hours. They were transferred into a closed titration cell with a volume of approximately 120 mL and titrated at 25 ± 0.1 °C with 0.1 M HCl containing 0.6 M NaCl. The titration cell was based on the systems described by Bradshaw and Brewer (1988) and Millero et al. (1993). The potential was followed with an electrode pair consisting of a ROSS (Orion Inc.) glass pH electrode and a ROSS AgCl reference electrode connected to a high precision digital voltmeter. The titration was controlled by a computer which waited for stable emf-readings before adding the next acid increment. The titration curve was analyzed with a modified GRAN-plot method described by Stoll et al. (1993) using the carbonic acid constants of Goyet and Poisson (1989) and taking into account the silicate and phosphate concentrations of the sample to obtain the titration alkalinity. The precision of the method was ± 2.0 µmol / kg determined by replicate analysis of samples. Standardization was accomplished with $NaCO_3$ standards in NaCl solutions corrected for the blank arising from impurities in the salt.

Underway pCO_2 was measured by the method of Schneider et al. (1992). Surface seawater was continuously pumped at a rate of 200 - 300 mL / min into a glass equilibrator with a volume of approximately 300 mL. The seawater was equilibrated with continuously circulating air entering the bottom of the equilibrator through a frit from a closed loop system. The latter included a heat exchanger to keep the air at the sample temperature, a filter and water trap, and an infra-red (IR) analyzer (Siemens, Ultrmat 5F) for the determination of the CO_2 content of the equilibrated air. The IR and the equilibrator temperature sensor were connected to a PC or to an analog recorder for data display and preservation. The time constant for the equilibration was about 3 minutes which corresponded to a spatial resolution of one half a mile with the ship steaming at 10 knots. Atmospheric air was periodically measured, and the system was calibrated every 12 hours using calibration gases with CO_2 mixing ratios of 252.5 and 412.8 ppm (v). Pressure corrections were made for the effect of water vapor on total pressure in the equilibrator and the pressure at the inlet of the IR analyzer, while the correction for the difference between in situ and measuring temperature was made according to Gordon and Jones (1973).

Accessing the Data Files

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FIGURE CAPTIONS

Figure 1. Station locations along the A1 / E WOCE Section during the Meteor 18 Cruise. (Alex you may want to distinguish between regular stations and CO_2 stations ?)

Figure 2. The distribution of the recording current meter moorings A to F along the section A1 / E overlaid on the observed temperature distributions. The current meter depths are indicated by a dot.

Figure 3. Color contour section plot of the C_T data obtained during the A1 / E transect in September 1991..