CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE R/V METEOR CRUISE 22/5 IN THE SOUTH ATLANTIC OCEAN (WOCE SECTION A10, DECEMBER 1992 - JANUARY 1993)

Contributed by

Kenneth M. Johnson[*], B. Schneider[**], L. Mintrop[***], Douglas W. R. Wallace[*]

[*] Oceanographic and Atmospheric Sciences Division
Brookhaven National Laboratory, New York, U.S.A.

[**] Institut fuer Ostseeforschung (IOW),
18111 Rostock-Warnemünde, Germany

[***] University of Bremen

Department of Geosciences
P.O. Box 330440
28334 Bremen, Germany

ABSTRACT

Johnson, K. M., B. Schneider, L. Mintrop, D.W. R. Wallace. 1996 Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R / V Meteor Cruise 22 in the South Atlantic Ocean (WOCE Section A10, December 1992 - January 1993).

This documentation discusses the procedures and methods used to measure total carbon dioxide (TCO_2), total alkalinity (TALK) at Hydrographic stations, as well as the underway partial pressure of CO_2 (pCO_2) during the R/V Meteor Cruise M22/5 in the South Atlantic Ocean (Section A10). Conducted as part of the World Ocean Circulation Experiment (WOCE), the cruise began in Rio de Janeiro on 27 December 1992, and ended after 36 days at sea in Capetown, South Africa on 31 January 1993. Instructions for accessing the data are provided.

TCO_2 was measured using two automated sample processors (SOMMA) for extracting CO_2 from seawater samples which were coupled to a Coulometer for detection of the extracted CO_2. The overall precision and accuracy of the analyses was ± 1.9 µmol / kg. Samples collected for total alkalinity were measured by potentiometric titration; precision was ± 2.0 µmol / kg. Underway pCO_2 was measured by Infra Red (IR) Photometry; precision was ± 2.0 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.

The R/V Meteor Cruise 22 data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of three oceanographic data files, three FORTRAN 77 data retrieval routine files, a readme file, and this printed documentation, which describes the contents and format of all files as well as the procedures and methods used to obtain the data.

Keywords: carbon dioxide; Coulometry, World Ocean Circulation Experiment; North Atlantic Ocean; Hydrographic measurements; alkalinity; pCO_2; carbon cycle

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

PART 1:

OVERVIEW

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. The need for this experiment arose from the serious concern over the rising atmospheric concentrations of carbon dioxide and its effect on the heat balance of the global atmosphere. The increasing concentrations of these gases may intensify the earth's natural greenhouse effect, and alter the global climate in ways that are not well understood. Carbon in the oceans is unevenly distributed because of poorly characterized and complex circulation patterns and biogeochemical cycles. 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 related parameters. Goals are 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 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 report discusses one such cruise: Meteor 22/5 (from Rio de Janeiro, Brazil to Capetown, South Africa from 27 December 1992 - 31 January 1993) which sampled along WOCE Zonal Section A10. This section is one of four contiguous zonal sections to be completed in the South Atlantic (A8, A9, A10, and A11) during the WOCE Survey. From these sections the largescale three-dimensional distribution of temperature, salinity, and chemical constituents, including the carbonate system parameters will be mapped. Knowledge of these parameters and their initial conditions will allow determination of heat and water transports as well as carbon transport. An understanding of these transports will contribute to the understanding of processes which are relevant for climate change. This section in the South Atlantic subtropical Gyre is especially relevant for CO_2 transport because it crosses both the Brazil and the Benguela Boundary Currents.

This report 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 aboard the R / V Meteor in December 1992 - January 1993 on cruise M22/5.

4

2. DESCRIPTION OF THE EXPEDITION

2.1 R/V *Meteor:* Technical Details and History

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
Basic Dimensions:	
Gross registered tonnage	3990
Net registered tonnage	1284
Displacement	4780 t
Overall Length	97.50 m
Beam	16.50 m
Draught (maximum)	5.60 m
Service 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
Propulsion	Diesel-electrical, tandem-motor = 2 x 1150 kW
Fuel consumption	~12.0 t IFO-80 per day at service speed
Maximum Cruise Duration	60 days
Nautical equipment	Integrated navigation system with data transfer to position computer, echosounder synchronization and supervision, and data-processing facility

Science Quarters	20 laboratories on main deck with ~ 400 m^2 of working space for multidisciplinary research

The R/V *Meteor* (I) was constructed in 1925, the first research and survey vessel of that name. Owned by the German navy, it was based in Wilhelmshaven. One of its first expeditions was the German Atlantic Ocean Expedition of 1925-27, which was organized by the Institute of Marine Research in Berlin. Thereafter, the vessel was used for German physical, chemical, and microbiological marine investigations and for German navy surveying and fisheries protection duties.

The R/V *Meteor* (II) was planned after the 1950s; it was operated by the Deutsche Forschungsgemeinschaft (German Science Community) in Bad Godesberg and by the Deutsches Hydrographisches Institut (German Hydrographic Institute) in Hamburg. Commissioned in 1964, R/V Meteor (II) participated in the International Indian Ocean Expedition.

The multipurpose R/V *Meteor* (III), used on the cruise described in this documentation, was completed in 1986 and replaced R/V *Meteor* (II). Based in Hamburg, it is used for German ocean research worldwide and for cooperative efforts with other nations researching in this field. The vessel serves scientists of all marine disciplines in all of the world's oceans.

2.2 R / V Meteor Cruise No. 18 Information

Ship Name	*Meteor*
Cruise / Leg	Cruise No. 22/5
Ports of call	Rio de Janeiro, Brazil to Capetown, South Africa
Dates	December 27, 1992 - January 31, 1993
Funding support	Deutsche Forschungs Gemeinshaft (DFG)
	U. S. Department of Energy (DOE)
Chief Scientist	Dr. Reiner Onken, IfMK
Master	Martin Kull

Parameters measured, institution, and responsible Investigators

Parameter	Institution	PI
CTD, Salinity, XBT	IfMK	R. Onken
Nutrients	IfMK	B. Schneider, H. Johannsen
Oxygen	IfMK	B. Schneider, H. Johannsen

Basin, the Walvis Ridge, and the Cape Basin. There was a small interruption in the work schedule to allow for a New Years Eve celebration between the hours of 10 pm and 4 am, and on 8 January nets laid by Spanish fishing boats on western edge of the Rio Grande Rise caused the *Meteor* to detour around them. However, meeting with the fishing boats also resulted in a trade between Captains in which the *Meteor* received fresh sword fish, yellow dolphin, and tuna. A small northward jog was made over the Walvis Ridge in order to sample around topographical features. The intervals between stations as the ship steamed eastward varied between 9 and 45 nm to limit the difference between the bottom depth at consecutive station depths to ≤ 1000 m. At 11 ° 30 ' E the ship veered slightly to the east-northeast in order to avoid the South African 200 nm exclusion zone because permission to sample in these waters had not been obtained. After this turn, the station resolution was reduced to 20 nm until the last station on the African shelf at a depth of approximately 200 m. The measurement phase concluded on January 28, 1993 and the *Meteor* steamed to Capetown where it arrived on the afternoon of January 30. Aside from some light rain and intermittent cloudiness at the beginning of the cruise, the weather remained mostly sunny with summer temperatures and calm seas throughout. Closer to the coast of Africa, swells of approximately 5 m originating from subantarctic low pressure areas were experienced, but without any loss of work time. The station locations are shown in Figure 1.

Two Single-Operator Multiparameter Metabolic Analyzers (SOMMA) were used on this cruise. One was supplied from BNL and one from the IfMK in Kiel (hereafter designated BNL and IfMK). In addition, 2 potentiometric alkalinity titrators from IfMK were run in parallel, and an IR-based system for measuring underway pCO_2 belonging to IfMK was deployed. Not counting duplicate or certified reference material (CRM) analyses, 1,425 samples were analyzed for C_T, in conjunction with tracer samples, from 57 of 100 CTD stations (57 %) occupied during the cruise. Counting duplicates and CRM analyses, 1,541 C_T analyses were made during the cruise. On 26 of the C_T stations 665 total alkalinity (A_T) samples were collected and analyzed. As on previous cruises, not all stations could be sampled for C_T and A_T because of the time required for analysis. However, the goal of 50 % coverage for C_T was surpassed, and on average 1.5 stations were sampled per day by the CO_2 group. The standard WOCE parameters (oxygen, nutrients, and salinity) were analyzed on all samples, and the tracer samples included CFC's, helium, tritium, and radiocarbon. The underway pCO_2 system operated continuously.

3. DESCRIPTION OF VARIABLES AND METHODS

3.1 Hydrography

Water samples were collected in 24 General Oceanics 10 l-Niskin bottles mounted on a Neil Brown Mark III CTD instrument provided by the IfMK. For stations ≥ 3500 m, two separate

8

CTD/rosette casts were made to get adequate coverage (n = 36). For stations < 3500 m, one CTD/rosette cast of up to 24 bottles was made. Surface currents down to 300 m, surface temperature, and surface salinity were measured continually during the cruise with a hull-mounted Acoustic Doppler Current Profiler (ADCP) and a Thermosalinograph. In between CTD stations, XBT's were routinely launched. Over the Boundary Currents XBT's were launched every half hour, and over the Benguela Current the XBT launches were supplemented with free-falling current profilers (XCP).

No serious problems were experienced with the CTD/rosette systems during this cruise. Repeated checks on board and several careful verifications using the complete bottle data sets have been carried out, and the sampling pressures assigned for each sample are to our knowledge correct. 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 follow the published guidelines in the WOCE Operations Manual (WHPO 91-1, 1991). **Salinity** calibrations were made using bottle salinities measured 1 - 2 days after collection on a Guildline Autosal model 8400A which was standardized with IAPSO water. The final salinity data are expected to be accurate to ± 0.002 on the Practical Salinity Scale (PSS). 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. The precision of the analyses determined from parallel analyses (n=10) of samples at and well below saturation is ± 0.4 %. The concentrations of **nitrate, nitrite, phosphate**, and **silicate** dissolved in seawater were determined on samples collected in high density polyethylene screw-capped bottles by a continuous-flow method with an autoanalyzer. Precision was: silicate ± 1.3 %; phosphate ± 1.5 %; nitrite/nitrate ± 1.1 %. Preweighed standards were used to prepare the nutrient working standards on board ship.

3.2   Total CO_2 (C_T)

3.2.1   General description of the Method

The **total carbon dioxide concentration** (C_T) was determined using two automated dynamic headspace sample processors (SOMMA) with coulometric detection of the CO_2 extracted from acidified samples. A description of the SOMMA-Coulometry System and its calibration can be found in Johnson et al., 1987; Johnson and Wallace, 1992; Johnson et al., 1993. A schematic diagram of the SOMMA analytical sequence is shown in Fig. 2, and further details concerning the coulometric titration can be found in Huffman (1977) and Johnson et al. (1985). Samples were collected in 300 mL precombusted (450 °C for 24 h) glass standard Biological Oxygen Demand

9

(BOD) bottles and analyzed for C_T during the cruise. On this cruise the samples were not poisoned with $HgCl_2$ as per normal operating procedure (DOE, 1994), but they were analyzed within 24 hours of collection. Before analysis, they were kept in darkness in a cold room, and subsequently thermally equilibrated for at least 3h to the analytical temperature. Analyses of duplicate samples separated in time by up to 8 hours showed no evidence of any significant biological consumption or production of CO_2 during storage. Certified Reference Material (CRM) were also routinely analyzed. The CRM were supplied by Dr. Andrew Dickson of the Scripps Institution of Oceanography (see DOE Handbook of Methods, 1994), and CRM from Batches 7 and 11 were available for this work (Batch 7, S = 37.120 and C_T = 1926.41 $\pm$ 0.82 μmol/kg; Batch 11, S = 38.5, C_T = 2188.77 μmol/kg). The CRM were made from filtered sterile salt solutions spiked with Na_2CO_3, and their C_T was determined by Vacuum - Extraction / Manometry in the laboratory of C. D. Keeling at SIO.

Seawater introduced from an automated To Deliver (TD) pipette into a stripping chamber was acidified and the resultant CO_2 from continuous gas extraction was dried, and coulometrically titrated on a model 5011 UIC Coulometer (Fig. 2). The Coulometers were adjusted to give a maximum titration current of 50 mA, and they were run in the counts mode (the number of pulses or counts generated by the Coulometer's voltage to frequency converter (VFC) during the titration was displayed). In the coulometer cell, the acid (hydroxyethylcarbamic acid) formed from the reaction of CO_2 and ethanolamine is titrated coulometrically (electrolytic generation of OH^-) with photometric endpoint detection. The product of the time and the current passed through the cell during the titration (charge in Coulombs) is 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.

Each system was controlled with an IBM compatible personal computer equipped with two RS232 serial ports, a 24 line Digital Input / Output (I / O) card, and a Analog to Digital (A / D) card. The latter were manufactured by Real Time Devices (State College, PA 16803). These were used to control the coulometer, barometer (BNL System only), 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 temperature of SOMMA components including the pipette, gas sample loops, and the coulometer cell. The SOMMA software was written in GWBASIC Version 3.20 (Microsoft Corp., Redmond, WA), and the instruments were driven from an options menu appearing on the PC monitor. With the coulometers operated in the counts mode, conversions and calculations were made using the

10

SOMMA software rather than the programs and the constants hardwired into the coulometer circuitry.

3.2.2 System Calibration and Calculations: BNL system

The BNL SOMMA-Coulometry System was calibrated with pure CO_2 using hardware consisting of an 8 port Gas Sampling Valve (GSV) with two sample loops of known volume (determined gravimetrically by the method of Wilke et al. (1993)) connected to a source of pure CO_2 through an isolation valve with the vent side of the GSV plumbed to a barometer (Fig. 2). When a gas loop was filled with CO_2, the mass (moles) of CO_2 contained therein was calculated by dividing the loop volume (V) by the Molar Volume of CO_2 at the ambient T and P. The Molar Volume of CO_2 ($V(CO_2)$) was calculated iteratively from an expression using the instantaneous barometric pressure (P), loop temperature (T), and the first virial coefficient $B(T$) for pure CO_2:

$$V(CO_2) = RT/P * (1 + B(T)/V(CO_2)) \tag{1}$$

The ratio of the calculated mass to that determined coulometrically, the gas calibration factor (Calfactor), was used to correct the subsequent titrations for small departures from 100 % recoveries (DOE Handbook of Methods, 1994). Pressure was measured with a barometer, model 216B-101 Digiquartz Transducer (Paroscientific, Inc. Redmond, WA) which is factory-calibrated for pressures between 11.5 and 16.0 psia. The standard operating procedure was to make gas calibrations daily for each newly prepared titration cell (normally, one cell per day and three sequential calibrations per cell).

The " to deliver " volume (V_{cal}) of the BNL SOMMA sample pipette was determined (calibrated) gravimetrically during the cruise by periodically collecting aliquots of deionized water dispensed from the pipette into preweighed serum bottles. The serum bottles were crimp sealed and returned to shore where they 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:

$$M_{vac} = W_{air} + W_{air}(.0012/d - .0012/8.0) \tag{2}$$

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 was:

11

$$V_{cal} = M_{vac} / d \tag{3}$$

The V_{cal} of the pipette for the BNL System was 20.6114 ± 0.0024 mL (n = 23) at a mean temperature of 14.67 °C (hereafter the calibration temperature t_{cal}). During the cruise the mean pipette temperature was 14.95 ± 0.97 °C, and the vast majority of samples were analyzed at a measurement temperature (t) which was within 1 °C of this calibration temperature. The sample volume (V_t) at the measured pipette temperature was calculated from the expression:

$$V_t = V_{cal} [1 + a_v (t - t_{cal})] \tag{4}$$

where a_v is the coefficient of volumetric expansion for pyrex-type glass (1×10^{-5} °C^{-1}), and t is the temperature of the pipette at the time of a measurement.

The BNL Coulometer was periodically electronically calibrated as described in Johnson et al. (1993, 1996) and DOE Handbook of Methods (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 fixed 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 at the factory, the electronic calibration procedure would yield a straight line passing through the origin (intercept = 0) with a slope of 1. For the BNL Coulometer, the mean electronic calibration slope during the M22/5 cruise was 0.999616 ± 0.000056 (n = 12, r.s.d. = 0.006 %) with an intercept of - 0.000533 µmol / min. 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 of micromoles of carbon titrated (M) from samples or the gas loops was:

$$M = [Counts / 4824.45 - (Blank * T_t) - (INT_{ec} * T_i)] / SLOPE_{ec} \tag{5}$$

where T_t was the length of the titration in minutes, Blank the system blank in µmol / min, INT_{ec} the intercept from electronic calibration in µmol / min, T_i the time in minutes during the titration where current flow was continuous, and $SLOPE_{ec}$ the slope from electronic calibration. Note that the slope obtained from the electronic calibration procedure applied for the entire length of the

12

titration, but the intercept correction applied only for the period of continuous current flow (usually 3 - 4 min) because the electronic calibration can only be carried out for periods of continuous current flow. The C_T concentration in μmol / kg was calculated from:

$$C_T = M * Calfactor * (1 / (V_t * rho)) * d_{Hg} * CF_{crm} \qquad (6$$

where Calfactor is the gas calibration factor, V_t is the " to deliver " sample volume from Eq. 4, rho is the density of sea water in g / mL at the measurement temperature and sample salinity calculated from the equation of state given by Millero and Poisson (1981), d_{Hg} is the correction for sample dilution with bichloride solution (for this cruise $d_{Hg} = 1.0$ for the BNL and Kiel analyses because $HgCl_2$ was not used), and CF_{crm} is a correction factor based on the daily liquid calibration by CRM analysis ($CF_{crm} = 1.0$ for all BNL analyses; no correction based on the CRM data).

The BNL SOMMA-Coulometry System was equipped with a conductance cell (Model SBE-4, Sea-Bird Electronics, Inc., Bellevue, WA 98005) for salinity measurement as described by Johnson et al. (1993). The conductance cell was factory calibrated, but SOMMA measured salinities were continuously compared with the CTD salinities to ensure that the salinities of the analyzed samples matched the assigned salinities. Generally, agreement between CTD and SOMMA salinities was 0.02 or better.

3.2.2.1 System Performance and Malfunctions: BNL system

A leak in the gas calibration hardware was discovered on January 12, 1993. It affected the gas calibrations by diluting the CO_2 calibration gas during the gas calibration procedure so that Calibration Factors (Calfactors) determined between December 28, 1992 and January 12 were in error by approximately + 0.1 %. These Calfactors caused an error of + 2 μmol / kg in the CRM analyses. Repairs were made on 12 January, and from this point through January 28 daily Calfactors were determined and used to calculate CRM and sample C_T. The mean Calfactor for the period 12 - 28 January was 1.004270 ± 0.000818 (n = 12). This Calfactor was used to recalculate the CRM and sample C_T for the period 28 December through 11 January.

3.2.3 System Calibration and Calculations: IfMK system

The IfMK System did not possess a gas calibration system, and gas calibration was not carried out during the cruise. This system was calibrated at the IfMK in Kiel prior to the cruise with liquid

standards (Na_2CO_3 solutions) according to the method of Goyet and Hacker (1992). A mean Calfactor (1.005 ± 0.07 %) was obtained in the laboratory from the ratio (true C_T / measured C_T). This was used in Eq. 6 to calculate the CRM and sample C_T throughout the cruise. During the calibration and at-sea work, the pipette volume, V_{cal} (also determined prior to the cruise), used for the IfMK System was 25.2347 mL at 20.02 °C (see Eq. 4). This "To Deliver" pipette volume was not redetermined gravimetrically during the cruise. Instead, an additional correction factor (CF_{crm}) based on the daily (cell-specific) CRM results was used to account for changes in pipette volume and/or system response by multiplying the sample C_T results by the ratio (see Eq. 6):

$$CF_{crm} = CRM \ (certified) \ / \ CRM \ (measured).$$

In summary, the IfMK System was calibrated as follows: a daily (cell-specific) correction factor (CF_{crm}) was applied to the water sample analysis results based on a laboratory determined constant Calfactor (1.005) and a constant value of V_{cal} (25.2347 mL at 20.02 °C). The IfMK Coulometer was not electronically calibrated during the cruise, and the theoretical response (Slope = 1, Intercept = 0) was assumed in Eq. 5 for all calculations. Note, however, that the CRM analysis results from the IfMK System (Fig. 2) were calculated with CF_{crm} = 1, in order that the variability of the CRM analyses and the magnitude of CF_{crm} can be assessed.

3.2.3.1   System Performance and Malfunctions: IfMK system

Problems were encountered with pinch valve tension particularly on pinch valve no. 4 (Fig. 2) of the IfMK System. This valve controls the delivery of sample to the stripper, and although it always operated, it affected the analytical results by periodically allowing additional sample to be injected into the stripper because the weak valve tension prevented the complete sealing of the tubing connecting the pipette to the stripper. The resulting errors for the CRM analyses were on the order of + 0.1 to 0.5 %. The valve tension was adjusted during the cruise, and the effect of these errors on data quality was minimized because poor results for the CRM analyses caused by the malfunctioning pinch valve caused us to repair the system before running any samples. However, the possibility remained that during the sample analyses periodic pinch valve failures may have occurred, and this has motivated us to carry out extensive quality control checks of the data described in the Quality Control-Quality Assurance (Section 3.2.4).

3.2.4   Quality Control-Quality Assurance (QC-QA)

3.2.4.1 Accuracy

The first phase of the Quality Control-Quality Assurance (QC-QA) procedure was an assessment of accuracy using the data from the CRM analyses. These data are shown in Figure 2 and summarized in Table 1. For BNL System, during the period 29/12/92 - 11/1/93 a constant Calfactor (1.004270) was used to calculate CRM C_T, while from 12/1/93 - 28/1/93 a daily (cell-specific) Calfactor was used to calculate CRM C_T. For the IfMK System, a constant Calfactor (1.005) was used for all calculations.

Table 1. Accuracy: Summary of CRM C_T determinations made during the M22/5 Cruise. Error refers to the mean difference between measured and certified C_T.

System	No. (n)	Batch[a]	Mean	S. D. (µmol / kg)	Error	Dates	Calfactor[b]	Outliers[c]
BNL	14	7	1926.68	0.65	+ 0.27	29/12/92 - 11/1/93	Constant	1
BNL	16	11	2188.66	0.89	- 0.11	12/1/93 - 28/1/93	Daily	0
IfMK	18	7	1928.09	1.57	+ 1.68	30/12/92 - 12/1/93	Constant	1
IfMK	11	11	2190.97	1.88	+ 2.20	13/1/93 - 28/1/93	Constant	3

[a] The CRM were from Batch 7 and 11 with salinities of 37.12 and 38.5, and a C_T of 1926.41 ± 0.82 µmol / kg (n = 13) and 2188.77 ± 0.56 µmol / kg (n = 5), respectively.

[b] See Section 3.2.4.1.

[c] An outlier is defined as a CRM analysis with an error ≥ 5.0 µmol / kg.

Mean errors on the BNL System were significantly lower than the consistently positive errors observed on the IfMK System. For the BNL System, an outlier was obtained on 4 January (CRM bottle no. 2), however, a second CRM (no. 275) run on the same cell gave a satisfactory result, and this cell was subsequently used to run samples. For the IfMK System, outliers were observed on 7 and 12 January (nos. 353 and no. 8). In each case, a second CRM analysis (nos. 318 and 244) gave satisfactory results, and the system was operated as normal. On 20 January two consecutive CRM analyses (no. 370 and 112) were classified as outliers, but a third CRM (no. 312) analysis gave a satisfactory result and the system was operated. Overall 5 of 64 CRM analyses from Table 1 (7.8 %) were classed as outliers, but 4 of these 5 outliers were obtained on the IfMK System which was further evidence for the slightly better performance of the BNL System. The greater number of outliers on the IfMK System could possibly due to the

malfunctioning of the IfMK pinch valve as described in section 3.2.3.1. In general, the CRM results on the BNL System were identical to the manometric reference analyses at SIO. The BNL System response remained very constant over the duration of the cruise (see Fig. 2) whether an average Calfactor (28/12/92 - 11/1/93) or a cell-specific Calfactor (12/1/93 - 28/1/93) was used to calculate CRM C_T. These results confirm a similar finding when mean Calfactors were used to calculate the M18 (WOCE Leg A1E) C_T data (Johnson et al., 1996).

3.2.4.2   Precision

The second phase of the QC-QA procedure was an assessment of sample precision on each system (instrument-specific precision). These precision data are given in Table 2. For these data, "within-sample" precision is the average absolute difference between two replicates analyzed from the same sample bottle, "between-sample" precision is the average absolute difference between duplicate sample bottles taken from the same Niskin Bottle, "between-Niskin" precision is the average absolute difference of analyses of samples taken from two Niskin Bottles which were closed at the same depth. The IfMK group assessed instrument-specific precision by periodically running 2 replicates from the same bottle ("within-sample"), while precision on the BNL System was assessed by running 1 replicate from each of 2 sample bottles filled from the same Niskin Bottle ("between-sample"). The pooled standard deviation (sp^2) is the square root of the pooled variance from the "between-sample" replicates (n = 2) according to Youden (1951):

$$Sp^2 = \sqrt{\frac{\sum\limits_{j=1}^{k} \left(\sum\limits_{i=1}^{n_j} \{x_{ij} - \bar{x}_j\}^2 - \{\sum\limits_{i=1}^{n_j}[x_{ij} - \bar{x}_j]\}^2 \Big/ n_i \right)}{\sum\limits_{j=1}^{k} n_j - k}}$$

where k is the number of samples analyzed, and $\sum\limits_{j=1}^{k} n_j$ - k are the degrees of freedom (d.f. in Table 2) for the calculation.

16

Table 2. Precision: Summary of sample precision for C_T analyses made during the M22/5 Cruise.

| System | Mean Precision and s.d. (μmol / kg) [a] | | | sp^2 |
	within-sample (n)	between-sample (n)	between-Niskin (n)	(k, n, d.f.)
BNL	(0)	1.04 ± 1.11 (53)	1.26 ± 1.41 (12)	1.07 (53, 106, 53)
IfMK	1.16 ± 1.62 (46)	0.98 ± 0.36 (6)	1.53 ± 2.04 (5)	0.73 (6, 12, 6)
Combined		1.03 ± 1.06 (59)	1.34 ± 1.55 (17)	1.04 (59, 118, 59)

[a] Mean precision is $[\sum_{x=1}^{n} abs (x_1 - x_2)] / n$, where n is the number of comparisons between duplicates analyses, x_1 and x_2. See text for explanation of sp^2.

Table 2 shows that there was no significant difference between the precision estimated using the three different methods, however, the standard deviation of the between-sample estimates was the lowest of the three methods. The same pattern was found for the Meteor 18 Cruise (WOCE Section A1E) C_T data when within-sample and between-sample precision were compared (see Johnson et al., 1996), and these data are also consistent with results for other WOCE Sections (Johnson et al., 1995; Johnson et al., 1996). For the instrument-specific sp^2, k is the number of between-sample samples analyzed on the same instrument, and n is the total number of replicates analyzed from k samples, and (n - k) is the degrees of freedom (d.f.).

3.2.4.3   Aliquots of the same sample analyzed on each system

The third phase of the QC-QA procedure was to assess the performance of the systems by comparing results from aliquots of the same sample analyzed on each system. The precedent was set for the M18 Cruise C_T data set because in that instance two SOMMA's were also run in parallel to generate the data set (Johnson et al., 1996). For the M18 data, a method-specific sp^2, assuming homogeneous variance, was calculated from aliquots of the same sample analyzed on each system. The same calculation was made for the applicable M22 samples, and the method-specific precision

17

(sp^2) for the M22 Cruise calculated from 31 such samples (k = 31, n = 2, d.f. = 31) was ± 1.92 μmol / kg. This is a more conservative estimate of overall cruise-wide precision than the instrument-specific precision shown in Table 2. For any measurement, irrespective of the instrument it was made on, the precision is ± 1.92 μmol / kg. This includes all sources of error-- random as well as any uncorrected systematic (bias).

Figure 3 is a histogram showing the frequency distribution of the differences between aliquots of 31 samples which were measured on both systems. The mean and standard deviation of the mean difference was +0.81 ± 2.46 μmol / kg (BNL - IfMK C_T results) with most of the differences falling within the ± 1.0 μmol / kg range (Fig. 3). The IfMK calibration procedure therefore appears to have been successful in eliminating any overall system bias seen for the IfMK CRM analyses given in Table 1. For the CRM, The BNL System (gas calibrated) gave more accurate results than the IfMK System (not gas calibrated), and no corrections have been made to any of the sample data analyzed on the BNL System based on the CRM results. In summary, the mean difference between aliquots of the same sample analyzed on both systems is < 1.0 μmol / kg, and

the method-specific pooled variance (sp^2 = ± 1.92 μmol / kg) calculated from Youden (1951) is a creditable estimate of precision and accuracy for the M22 data set generated by two systems run in parallel but calibrated differently.

3.2.4.3 Aliquots of the same sample analyzed at-sea and on-shore

The fourth step in the QA-QC procedure, the at-sea to on-shore comparison, resulted from when replicates of of the same sample were analyzed in real time at sea and later, after storage, on-shore. This procedure was repeated a total of 14 times with replicates collected at 7 stations. The on-shore analyses were made by Vacuum Extraction / Manometry in the laboratory of Dr. Charles Keeling at SIO. The results of the comparison are given in Table 3.

Table 3. Comparison of at-sea analyses of C_T by coulometry and the on-shore analyses of C_T by manometry on aliquots of the same sample. The CRM error refers to the difference between the determined and certified CRM C_T for the specific coulometer cell used to titrate the sample at-sea. Storage refers to the time in months elapsed between sample collection and on-shore analysis by manometry.

Date/Station/Niskin (1993) (no.)	Depth (m)	At-sea (µmol / kg)	On-shore (µmol / kg)	Storage (mos.)	Diff.	CRM error
BNL Analyses						
13/1 / 48 / 318	10.2	2045.68	2047.49	11	- 1.81	0.18
13/1 / 48 / 308	3002.0	2188.44	2189.98	10	- 1.54	0.18
15/1 / 54 / 323	10.7	2044.96	2047.51	5	- 2.55	- 0.76
15/1 / 54 / 301	2808.1	2200.83	2202.68	5	- 1.85	- 0.76
19/1 / 68 / 323	10.4	2064.83	2068.02	10	- 3.19	- 0.14
19/1 / 68 / 307	3002.9	2200.10	2203.27	10	- 3.17	- 0.14
21/1 / 76 / 208	12.4	2057.86	2060.61	4	- 2.75	1.12
21/1 / 76 / 306	3003.1	2203.31	2207.06	4	- 3.75	1.12
24/1 / 85 / 213	11.8	2041.48	2047.61	3	- 6.13	- 0.68
24/1 / 85 / 312	3002.3	2200.73	2207.66	4	- 6.93	- 0.68
27/1 / 93 / 213	12.0	2029.99	2033.69	3	- 3.70	- 0.39
27/1 / 93 / 305	3003.5	2200.52	2005.61	3	- 5.09	- 0.39
mean (n = 12)				6	- 3.54	- 0.11
s.d				± 3	± 1.71	± 0.69
IfMK Analyses						
17/1/ 62 / 208	12.0	2046.45	2054.22	4	- 7.77	2.04
17/1/ 62 / 307	3004.0	2190.57	2202.12	5	- 11.55	2.04
mean				4	- 9.66	
s.d.				± 1	± 2.67	

On the BNL System the initial comparisons (13 Jan - 15 Jan, n = 4, mean error - 1.93 µmol / kg) were consistent with the precision and accuracy (± 1.92 µmol / kg) of the method, but larger differences were observed after 15 Jan. The mean difference for the cruise was - 3.54 µmol / kg (for the M18 Cruise the corresponding results were - 2.13 µmol / kg (n = 7) with a method-

specific accuracy of ± 1.65 μmol / kg). Overall the ship-to-shore difference is clearly not depth dependent. The poorest results were the very negative differences for samples collected on 17 Jan at Station 62 and run on the IfMK System. We have other reasons to strongly suspect shipboard analyses from Station 62 on the IfMK System (see Section 3.2.4.5) so that these samples have been averaged separately in Table 3. Note that only 3 of the 12 differences were within the analytical precision of the shipboard method and these occurred early on in the cruise, 6 of the 12 were essentially within 2 standard deviations (± 3.84 μmol / kg), but 3 differed by more than 2 s.d. All of the differences were negative. The errors for the CRM are nowhere near as large as the ship to shore differences. The length of time the samples were stored prior to analysis on-shore is also not apparently correlated with the at-sea vs on-shore differences. The reason for the difference between shipboard and shore-based analyses remains to be determined.

3.2.4.5 Multiple Linear Regression

The data given in Tables 2 and 3 suggested that further quality control-quality assurance (QC-QA) analysis of the data was justified. As described above, the two SOMMA systems used during Meteor 22 employed different calibration strategies, and the number of replicate samples analyzed on both instruments was insufficient to assess bias on a station-by-station basis. As an additional cross-check on the inter-comparability of C_T concentrations measured using the two analytical systems we compared the correlation of the C_T with other measured oceanographic parameters. Brewer et al. (1995) and Wallace (1995) have previously noted that strong multivariate relationships exist between C_T and other Hydrographic parameters (e.g. temperature, salinity, oxygen and dissolved nutrients). These relationships are remarkably robust over basin-scales and have been used to examine the temporal build-up of CO_2 in the oceans (Wallace, 1995; Wallace et al., 1996) and to interpolate sparse data (Brewer et al., 1995).

Our approach was as follows: multiple linear regressions were initially performed for C_T data collected from three geographical sections of the Meteor 22 cruise. Earlier work had suggested that regression fits varied slightly from one ocean basin to another. The section was therefore broken down into three groups of stations: those occupied in Zone 1 defined as being west of 13 °W (west of the Mid-Atlantic Ridge; southern Brazil Basin); stations occupied in Zone 2 defined as being between 13 ° W and 3 °E (between the Mid-Atlantic and Walvis Ridges; Southern Angola Basin) and stations occupied in Zone 3 defined as being east of 3 °E (east of the Walvis Ridge; Northern Cape Basin). For each group of stations, all samples collected from below 200m for which C_T had been measured (on either system) were extracted and a stepwise multiple linear regression was performed with C_T being the dependent variable and the wide range of other measured Hydrographic parameters as independent variables. The regression models determined that only

potential temperature, salinity, apparent oxygen utilization (AOU) and silicate were significant predictors (this is the same choice of parameters as found previously by Wallace (1995) for a section along 19 °S). In addition, a single regression was performed for all of the data collected below 200 m from the entire section. The regression parameters for these four different geographical groupings of stations are presented in Table 4. For each of these four geographical groupings, two sets of regression coefficients are presented: one was derived from a regression that employed the measured silicate concentration as an independent variable and one for a regression that did not use silicate as a predictor.

Table 4. Summary of initial multiple regression results with and without silicate as an independent variable. See text for definition of Zone.

Regression No.	Longitude Range	Intercept	Coefficients Pot. Temp.	Salinity	AOU	SiO$_4$	Std. Error
0A	Entire Section	1987.32	-4.296	4.045	0.620	0.482	4.37
0B	Entire Section	1370.40	-6.254	22.038	0.827	-.-	6.88
1A	Zone 1	1975.58	-4.259	4.370	0.633	0.462	4.77
1B	Zone 1	1395.65	-5.957	21.178	0.864	-.-	7.12
2A	Zone 2	2858.72	-2.531	21.163	0.327	1.126	4.44
2B	Zone 2	1316.58	-6.623	23.822	0.754	-.-	4.42
3A	Zone 3	2201.00	-3.949	-2.246	0.621	0.538	2.65
3B	Zone 3	1540.28	-7.049	17.431	0.764	-.-	7.76

This initial exercise was not particularly satisfactory as illustrated by the regression coefficients which varied significantly from one geographical zone to another, and depending on whether silicate was employed as a predictor (Table 4). For example the AOU coefficient varied from 0.33 to 0.63 when silicate was employed as an independent variable; it reached as high as 0.86 when silicate was not used as a predictor. The salinity coefficient was even more variable ranging from -21 to +24. In general the potential temperature, AOU and salinity coefficients were stable across the geographical groupings when silicate was not used in the regression: the inclusion of silicate caused the other coefficients to vary significantly. Use of silicate as a predictor could also shift the coefficients for the other parameters outside of their "oceanographically reasonable" ranges. For example, the AOU coefficient if interpreted to reflect the respiratory quotient for organic material, should be of order 0.68 (Takahashi et al., 1985) 0.69 (Anderson and Sarmiento, 1994) or 0.77 (Redfield et al., 1963). Clearly the AOU coefficient derived from regression # 2A falls well

21

outside this accepted range. Likewise, even the sign of the salinity coefficient is variable. "Oceanographic reasoning" suggests that there should be a positive partial correlation between C_T and salinity because of the strong positive correlation between carbonate alkalinity and salinity in the ocean (the countervailing tendency of CO_2 gas solubility to decrease with increasing salinity is a relatively minor effect). The use of silicate did significantly reduce the overall standard error of the predictions (Table 4), and eliminated or markedly reduced certain systematic patterns in the distribution of the residuals with depth (results not shown).

In order to examine further the influence of silicate, we plotted the residuals evaluated from regressions based upon only potential temperature, salinity and AOU against silicate. This plot (not shown) showed that for silicate concentrations between 0 and ~40 μmol kg^{-1}, the residuals averaged zero and there was no discernible trend; however for silicate concentrations greater than ~40 μmol kg^{-1} there was a very clear positive correlation of the residuals with silicate. On the basis of this we decided to define a new parameter, the "silicate index" (I_{Si}) as:

$$I_{Si} = ([SiO_4] > 40) * ([SiO_4] - 40)$$

This index is equal to zero for SiO_4 concentrations less than 40 μmol kg^{-1}, and is equal to ($[SiO_4]$ - 40) when silicate is greater than or equal to 40 μmol kg^{-1}.

The results of regressions using the silicate index, potential temperature, salinity and AOU as independent variables, are presented in Table 5. It can be seen that use of the silicate index, rather than the silicate concentration, makes the regression coefficients for the other parameters much more consistent from one geographical zone to another (cf. Table 4). Given the overall consistency of fit, we felt confident in using a single regression equation to predict the C_T over the entire section (Regression #0, Table 5).

The distribution of residuals arising from this single section-wide regression equation are presented separately for the three geographical zones in Figure 4. Separate symbols are employed for the residuals derived from measurements made on the BNL and Kiel SOMMAs. In general, there is little or no systematic structure apparent in the residual distribution (except perhaps at very low C_T concentrations which are found close to the surface where seasonal effects may be significant), and the regression fits the data from all three zones reasonable well.

Table 5. Summary of multiple regression results when the Silicate Index (I_{Si}) was used as a predictor. See text for definition of Zone and the Silicate Index.

Regression No.	Longitude Range	Intercept	Coefficients Pot. Temp.	Salinity	AOU	I_{Si}	Std. Error
0	Entire Section	1706.33	-5.747	12.474	0.722	0.434	4.59
1	Zone 1	1704.61	-5.565	12.443	0.746	0.422	4.98
2	Zone 2	1863.67	-6.075	8.217	0.618	0.770	4.17
3	Zone 3	1964.15	-5.867	5.135	0.688	0.464	2.99

In order to assess the intercomparability of C_T measurements made on the two SOMMAs on a station-by-station basis, we have plotted (Fig. 5) the mean residual (calculated for each station) based upon this section-wide fit. This plot permits an assessment of the overall consistency of the measured C_T with the other measured Hydrographic parameters over the entire cruise. The plot demonstrates the following:

(1)   There is some slight spatial structure to the station-mean residuals, with the mean residual in Zone 2 (12.9 °W < longitude < 3°E) being ~1-2 μmol / kg higher than for the rest of the section. We saw no corresponding trend in the CRM analyses on the BNL system (Fig. 2) and we therefore hypothesize that this slight variation is "real" and is associated with different origins for water masses in this zone.

(2)   In general, there is no consistent difference between the station-mean residuals based on measurements made with the BNL and IfMK SOMMAs. The overall consistency of the two sets of measurements appears to be better than $\pm$ 2 μmol / kg, which is consistent with the accuracy and precision bounds ($\pm$ 1.9) for the overall data set given previously in Section 3.2.4.3. This confirms that the cruise-wide calibration of the C_T data analyzed with the two instruments was nearly identical.

(3)   Three stations (625, 46, and 62) appear to be outliers from this overall pattern. These stations have a mean residual that is significantly different from the overall mean of the station-mean residuals analyzed with the BNL SOMMA. All of these three stations were measured using the Kiel SOMMA. While we cannot rule out the possibility that these deviations arise from errors in the measurement of the independent variables used in the regressions (e.g. the oxygen or silicate analyses or from "real" oceanographic variability), we hypothesize that they are the result of calibration error of the C_T analysis at these stations.

23

Given the approach used to calibrate the IfMK SOMMA (see Section 3.2.3), such deviations could arise from a single incorrect analysis of a Certified Reference Material which would cause the correction factor (CF_{crm} in Eq. 6) for an entire station to shift based on an incorrect analysis. The BNL SOMMA analyses were less prone to such errors because the primary calibration was based on analyses of pure CO_2 (gas calibration) with the Certified Reference Material analyses being used as an independent cross-check on this primary calibration. With this approach, any calibration errors that may lead to systematic errors for an entire station are more likely to be identified and corrected.

The residual intercomparison confirms that the overall quality of the combined BNL and IfMK data set is very high. However, three anomalous stations were identified. The C_T results at Station 62 appear to be low by 5 - 7 μmol / kg. This station was also sampled for on-shore manometric analyses, and the results in Table 3 confirm that whereas other stations had a mean (ship-shore) difference of - 3.54 μmol / kg ($\pm$ 1.71 μmol / kg), the shipboard analyses from station 62 were 8 - 12 μmol / kg lower than the shore-based results. We therefore conclude from these two independent lines of evidence that the Station 62 results are too low and they **have been flagged as incorrect in the data file.** Based on the residual analysis, C_T results at Station 46 may also be low by ~ 2 - 4 μmol / kg and C_T results at Station 625 maybe high by as much as 14 μmol / kg. However we have no independent way to assess the data from these stations, and the anomalous residual could be "real" due to error in the predictor variables. Therefore the C_T data from these stations have been flagged as "questionable". Only these three stations have been flagged: the data collected at the remaining 51 stations which were sampled for C_T appears to be internally consistent.

3.3 Total Alkalinity (A_T)

A total of 665 samples were collected in 500 mL bottles from 26 stations 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. No reference material (CRM) were analyzed during this cruise for alkalinity.

3.4 Underway pCO_2

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 and the pressure at the inlet of the IR analyzer, while the correction for the small difference between in situ and measuring temperature was made according to Gordon and Jones (1973).

3.5 Secchi disk readings

Between December 30, 1992 and January 28, 1993 as the ship moved eastward Secchi disk readings were made during daylight hours when the opportunity arose. These data are given in Table 6.

Table 6. Secchi Disk readings made during the M22/5 Cruise.

Date	Local Time	Latitude (° S)	Longitude (- °W, + °E)	Conditions	Depth (m)
30.12	1530	27° 55'	- 46° 40'	good vision	25.0
31.12	1200	28° 05'	- 45° 56'	clear	30.0
01.01	1700	28° 50'	- 43° 35'	cloudy	19.0
03.01	1230	30° 00'	- 40° 00'	cloudy, dry	26.0
05.01	1530	30° 00'	- 36° 10'	sunny, dry	33.0
06.01	1300	30° 00'	- 34° 00'	partly cloudy	30.0
07.01	1300	30° 00'	- 32° 00'	hazy	19.0
09.01	1600	30° 00'	- 27° 00'	hazy	29.0
15.01	1800	30° 00'	- 13° 40'	clear, sunny	31.0
16.01	1300	30° 00'	- 11° 40'	clear, sunny	42.0
18.01	1300	30° 00'	- 07° 00'	clear, sunny	42.0
20.01	1300	30° 00'	- 01° 00'	clear, sunny	37.0
23.01	1630	29° 45'	+ 05° 06'	good	32.0
28.01	1400	28° 37'	+ 14° 41'	sunny	17.0
28.01	1700	28° 30'	+ 15° 00'	sunny	7.0

Accessing the Data Files

Alex ....

REFERENCES

Anderson, L. A. and J. L. Sarmiento. 1994. Redfield ratios of remineralization determined by nutrient data analysis. Global Biogeochem. Cycles, 8: 65 - 80

Bradshaw A. L. and Brewer, P. G. 1988. High precision measurements of alkalinity and total carbon dioxide in seawater by potentiometric titration-1. Presence of unknown protolyte (s) ? Mar. Chem., 23: 69 - 86.

Brewer, P. G., D. M. Glover, C. Goyet and D. K. Shafer. 1995. pH of the North Atlantic Ocean: improvements to the global model for sound absorption in seawater. J. Geophys. Res, 100: 8761 - 8776.

Brewer, P. G., Goyet, C., and Dyrssen, D. 1989. Carbon dioxide transport by ocean currents at 25 °N latitude in the Atlantic Ocean. Science, 246: 477 - 479.

Bryden, H. L. and Hall, M. M. 1980. Heat transport by ocean currents across 25 °N latitude in the North Atlantic Ocean. Science, 207: 884.

Carpenter, J. H. 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. Limnol. Oceanogr., 10: 141 - 143.

Culberson, C. H., Williams, R. T., et al. 1991. A comparison of methods for the determination of dissolved oxygen in seawater. WHP Office Report, WHPO 91-2, 15 pp.

DOE Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2.0. 1994. A. G. Dickson and C. Goyet (eds.). Available from Andrew G. Dickson, Marine Physical Laboratory, 0902, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0902.

Gordon, L. I. and Jones, L. B. 1973. The effect of temperature on carbon dioxide partial pressure in seawater. Mar. Chem., 1: 317 - 322.

Goyet, C. and Poisson, A. 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. Deep-Sea Res., 36: 1635 - 1654.

Goyet, C. and Hacker, S. D. 1992. Procedure for calibration of a coulometric system used for total inorganic carbon measurements of seawater. Mar. Chem., 38: 37 - 51.

Huffman, E. W. D., Jr. 1977. Performance of a new automatic carbon dioxide coulometer. Microchemical J., 22: 567 - 573.

Johnson, K. M., King, A. E., and Sieburth, J. McN. 1985. Coulometric TCO$_2$ analyses for marine studies: An introduction. Mar. Chem., 16: 61 - 82.

Johnson, K. M., Sieburth, J. McN, Williams, P. J. leB., Brändström, L. 1987. Coulometric TCO$_2$ analysis for marine studies: Automation and calibration. Mar. Chem., 21: 117-133.

Johnson, K. M. and Wallace, D. W. R. 1992. The single-operator multiparameter metabolic analyzer for total carbon dioxide with coulometric detection. DOE Research Summary No. 19. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, TN.

Johnson, K. M., Wills, K. D., Butler, D. B., Johnson, W. K., Wong, C. S. 1993. Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector. Mar. Chem.. 44: 167 - 187.

Johnson, K. M., Schneider, B., Mintrop, L., and Wallace, D. W. R. 1996. Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/V Meteor cruise 18/1 in the North Atlantic Ocean (WOCE Section A1E, September 1991). NDP-056. Carbon Dioxide Information Analysis Center (CDIAC), Oak Ridge National Laboratory, Oak Ridge, TN 37831-6335.

Millero, F. J. and Poisson, A. 1981. International one-atmosphere equation of state for sea water. Deep-Sea Res., 28: 625 - 629.

Millero, F. J., Zhang, J.-Z., Lee, K., and Campbell, D. M. 1993. Titration alkalinity of seawater. Mar. Chem., 44: 153 - 165.

Redfield, A. C., B. H. Ketchum, and F. A. Richards. 1963. The influence of organisms on the composition of seawater, in The Sea, vol. 2, edited by M. N. Hill, pp. 26 - 77, John Wiley, New York.

Roemmich, D. and Wunsch, C. 1985. Two transatlantic sections: meridional circulation and heat flux in the subtropical North Atlantic Ocean. Deep Sea Res., 32: 619 - 664.

Schneider, B., Kremling, K., and Duinker, J. C. 1992. CO_2 partial pressure in northeast Atlantic and adjacent shelf waters: Processes and seasonal variability. J. Mar. Systems, 3: 453 - 463.

Stoll, M. H. C., Rommets, J. W., and De Baar, H. J. W. 1993. Effect of selected calculation routines and dissociation constants on the determination of total carbon dioxide in seawater. Deep-Sea Res., 40: 1307 - 1322.

Takahashi, T., W. S. Broecker, and S. Langer. 1985. Redfield ratio based on chemical data from isopycnal surfaces. J. Geophys. Res., 90: 6907 - 6924.

Wallace, D. W. R., K. M. Johnson, J. Holfort, and B. Schneider. 1996. Detection of the changing CO_2 inventory in the ocean. US WOCE Report. US WOCE Implementation Report Number 8, Texas A&M University, College Station TX, 48 pp.

Wallace, D. W. R. 1995. Monitoring global ocean carbon inventories. Ocean Observing System Development Panel, Texas A&M University, College Station, TX, 54 pp.

Wilke, R. J., Wallace, D. W. R., and Johnson, K. M. 1993. A water-based, gravimetric method for the determination of gas sample loop volume. Anal. Chem., 65: 2403 - 2406.

Youden, W. J. 1951. Statistical Methods for Chemists. Wiley, New York, 126 pp.

FIGURE CAPTIONS

Figure 1. Station locations along the A10 WOCE Section during the Meteor 22 Cruise. (Alex you may want to distinguish between regular stations and CO_2 stations ?)

Figure 2. The distribution of difference between the measured and certified value of the CRM analyzed by the BNL SOMMA-Coulometry System (closed circles) and the IfMK SOMMA-Coulometry System (open squares) during the Meteor 22 Cruise. The IfMK results have been calculated based on the pre-cruise calibration only (see text).

Figure 3. A histogram showing the frequency and distribution of the magnitude of the differences for 31 samples for which aliquots were analyzed on both measurement systems (BNL and IfMK) during the Meteor 22 Cruise.

Figure 4. Residuals (observed - predicted) of C_T versus the observed C_T concentration for three separate geographical groupings of stations occupied during Meteor 22. The residuals were evaluated against a multiple linear regression equation derived from all the C_T data collected during the cruise (at depths > 200 m). The independent variables used in the regression were potential temperature, salinity, apparent oxygen utilization (AOU) and a silicate index (I_{Si}). The regression coefficients used were those presented for regression #0 in Table 6.

Figure 5. The mean C_T residual (observed - predicted) for each station occupied during Meteor 22; residuals were evaluated using a section-wide multiple linear regression (coefficients given for regression #0 in Table 6). The error bars denote the 95% confidence interval of the station-mean residual. Filled symbols reflect stations analyzed using the BNL SOMMA, open symbols reflect analyses using the Kiel SOMMA. The demarcation of three geographical zones reflecting three separate ocean basins sampled during the cruise are denoted with the vertical lines. The horizontal lines represent the cruise-wide mean and 95% confidence intervals calculated for the station-mean residuals using the BNL SOMMA results only.
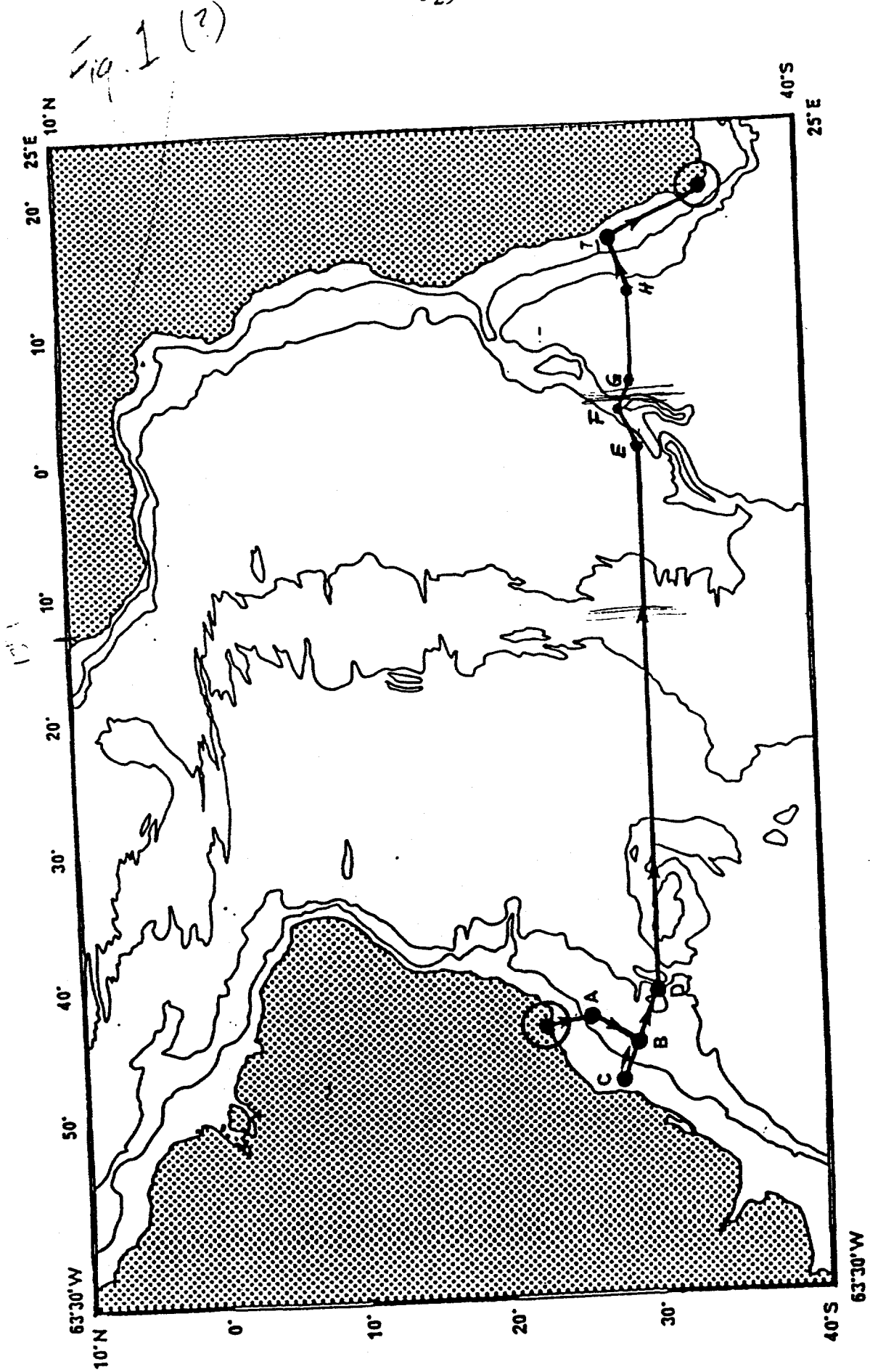
31

Fig. 6 : Cruise track M 22/5. The depth contours represent the 2000 and 4000 m isopleths.
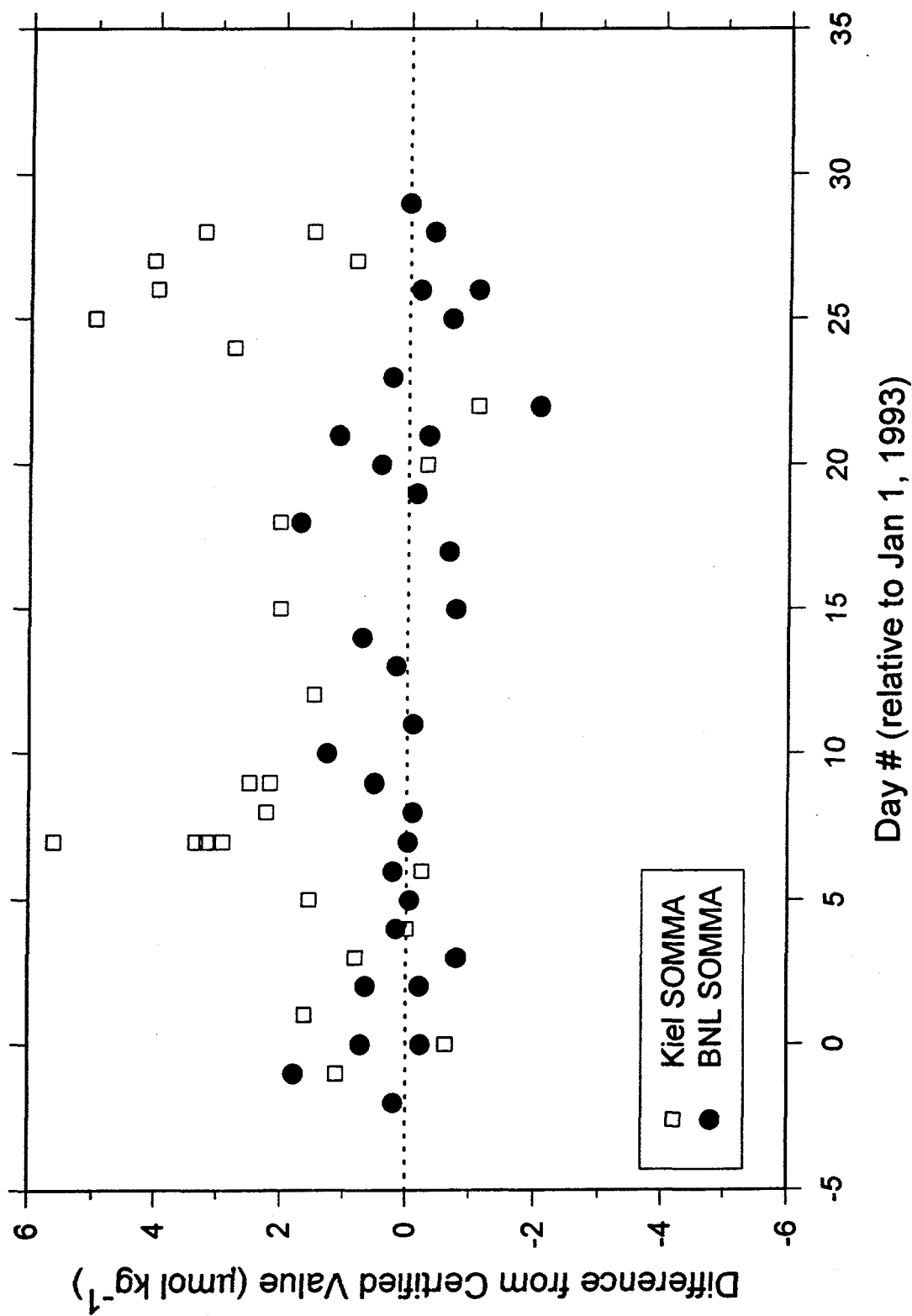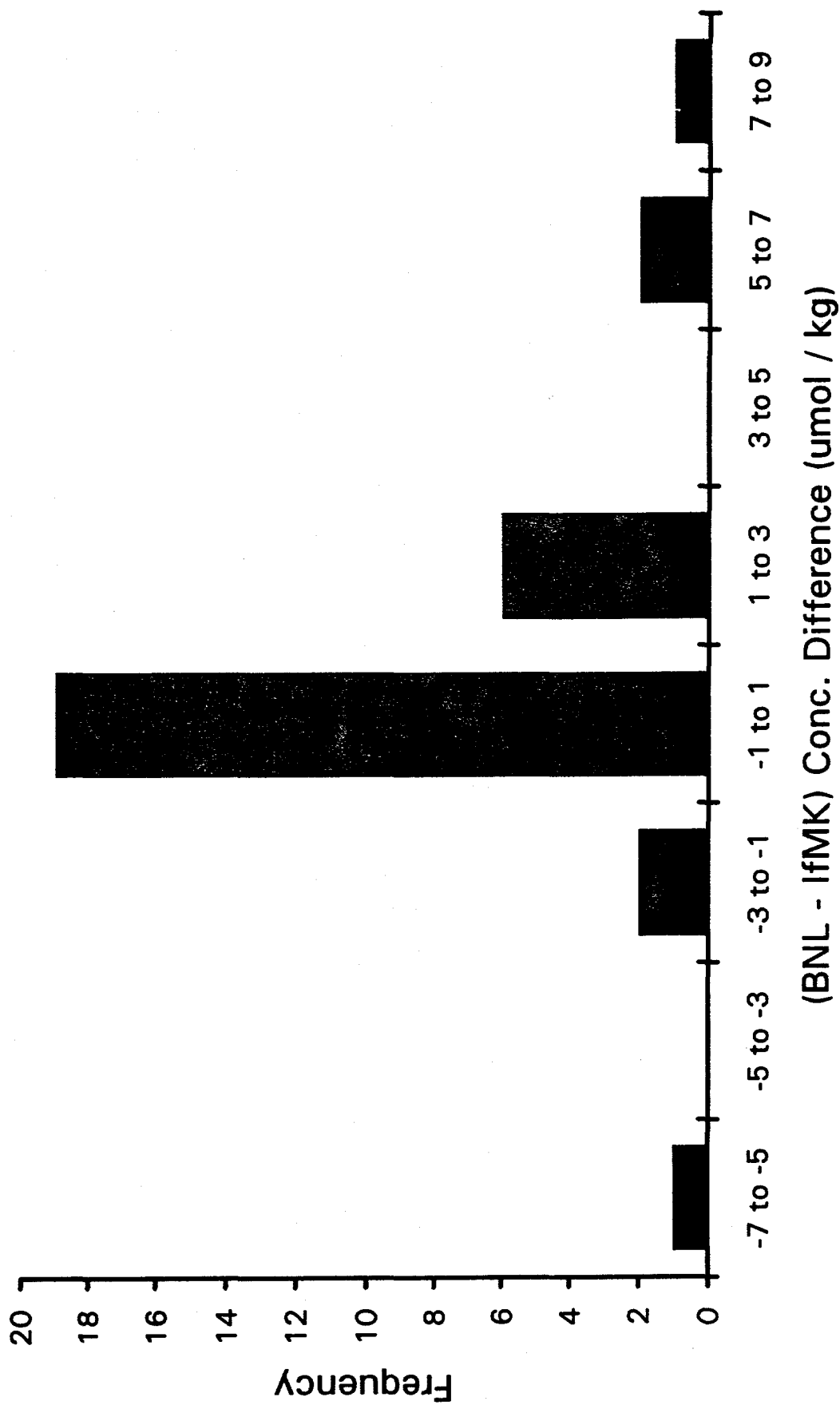
Meteor 22; WOCE A10

Fig. 2.

Chart1 3/11/97

Fig. 3

Frequency vs. (BNL - IfMK) Conc. Difference (umol / kg)

Frequency axis: 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20

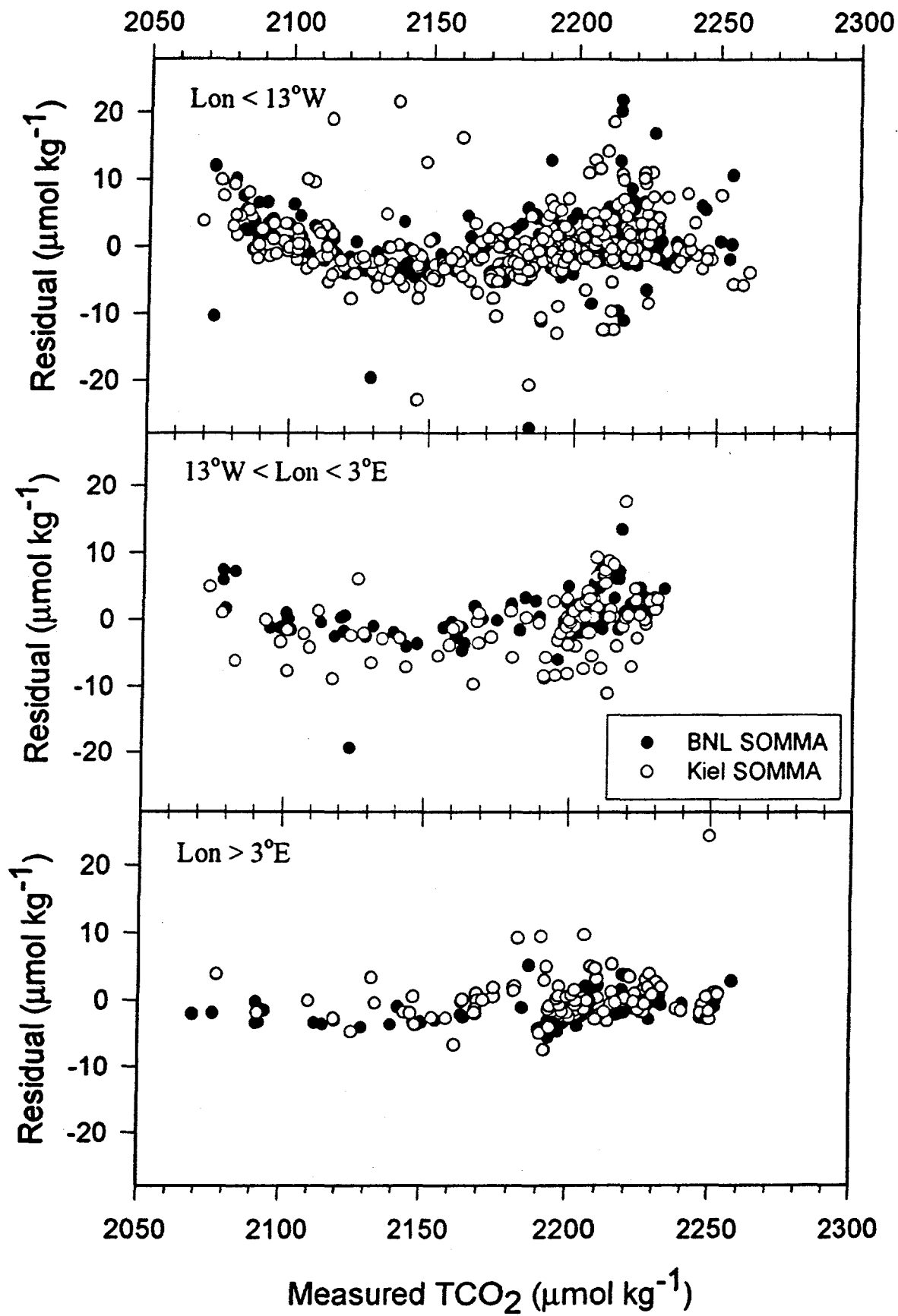X-axis categories: -7 to -5, -5 to -3, -3 to -1, -1 to 1, 1 to 3, 3 to 5, 5 to 7, 7 to 9

Fig. 4

Fig. 5

Meteor 22; Cruise-Wide Regression

Station-Mean Residual (μmol kg⁻¹) — $\text{Station-Mean Residual (}\mu\text{mol kg}^{-1}\text{)}$

Station Number

Zone 1
lon < 13°W

Zone 2
13°W < lon < 3°E

Zone 3
lon > 3°E

Stn. 625

Stn. 46

Stn. 62

BNL SOMMA
Kiel SOMMA