Carbon Dioxide, Hydrographic, and Chemical Data Obtained During the R/V *Hespérides* Cruise in the Atlantic Ocean

(WOCE Section A5, July 14 – August 15, 1992)
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CARBON DIOXIDE, HYDROGRAPHIC, AND CHEMICAL DATA OBTAINED DURING THE R/V HESPERIDES CRUISE IN THE ATLANTIC OCEAN (WOCE SECTION AS, JULY 14 – AUGUST 15, 1992)

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Environmental Sciences Division
Publication No. 4988

Date Published: June 2000

Prepared for the
Environmental Sciences Division
Office of Biological and Environmental Research
U.S. Department of Energy
Budget Activity Numbers KP 12 04 01 0 and KP 12 02 03 0

Prepared by the
Carbon Dioxide Information Analysis Center
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6335
managed by
UT-BATTENELL, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725
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ACKNOWLEDGMENTS

The authors wish to acknowledge the National Oceanographic and Atmospheric Administration, the Oceanographic Section of the National Science Foundation, the U.S. Department of Energy, and the Office of Naval Research for supporting this study.
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<td>$^{14}$C</td>
<td>radiocarbon</td>
</tr>
<tr>
<td>ADCP</td>
<td>acoustic Doppler current profiler</td>
</tr>
<tr>
<td>ASCII</td>
<td>American Standard Code for Information Interchange</td>
</tr>
<tr>
<td>CDIAC</td>
<td>Carbon Dioxide Information Analysis Center</td>
</tr>
<tr>
<td>CEAB</td>
<td>El Centro de Estudios Avanzados de Blancas</td>
</tr>
<tr>
<td>CFC</td>
<td>chlorofluorocarbon</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>CRM</td>
<td>certified reference material</td>
</tr>
<tr>
<td>CTD</td>
<td>conductivity, temperature, and depth sensor</td>
</tr>
<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
</tr>
<tr>
<td>cmf</td>
<td>electromotive force</td>
</tr>
<tr>
<td>FCMLP</td>
<td>Facultad de Ciencias del Mar</td>
</tr>
<tr>
<td>fCO$_2$</td>
<td>fugacity of CO$_2$</td>
</tr>
<tr>
<td>FTP</td>
<td>file transfer protocol</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GMT</td>
<td>Greenwich Mean Time</td>
</tr>
<tr>
<td>GO</td>
<td>General Oceanics</td>
</tr>
<tr>
<td>GPS</td>
<td>global positioning system</td>
</tr>
<tr>
<td>IEO</td>
<td>Instituto Español de Oceanografía</td>
</tr>
<tr>
<td>IIIM</td>
<td>Instituto de Investigaciones Marinas</td>
</tr>
<tr>
<td>IPO</td>
<td>WOCE International Program Office</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>JGOFS</td>
<td>Joint Global Ocean Flux Study</td>
</tr>
<tr>
<td>LDEO</td>
<td>Lamont-Dobert Earth Observatory</td>
</tr>
<tr>
<td>NBIS</td>
<td>Neil Brown Instruments Systems</td>
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<tr>
<td>NDP</td>
<td>numeric data package</td>
</tr>
<tr>
<td>nm</td>
<td>nautical mile</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
</tr>
<tr>
<td>PSS</td>
<td>practical salinity scale</td>
</tr>
<tr>
<td>QA</td>
<td>quality assurance</td>
</tr>
<tr>
<td>RSMAS</td>
<td>Rosenstiel School of Marine and Atmospheric Science</td>
</tr>
<tr>
<td>RTD</td>
<td>resistive temperature device</td>
</tr>
<tr>
<td>R/V</td>
<td>research vessel</td>
</tr>
<tr>
<td>SIO</td>
<td>Scripps Institution of Oceanography</td>
</tr>
<tr>
<td>TALK</td>
<td>total alkalinity</td>
</tr>
<tr>
<td>TCO$_2$</td>
<td>total carbon dioxide</td>
</tr>
<tr>
<td>UPC</td>
<td>Universidad Politecnica de Cataluña</td>
</tr>
<tr>
<td>URL</td>
<td>universal resource locator</td>
</tr>
<tr>
<td>WCRP</td>
<td>World Climate Research Program</td>
</tr>
<tr>
<td>WHOI</td>
<td>Woods Hole Oceanographic Institution</td>
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<tr>
<td>WHPO</td>
<td>WOCE Hydrographic Program Office</td>
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<tr>
<td>WOCE</td>
<td>World Ocean Circulation Experiment</td>
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ABSTRACT


This data documentation discusses the procedures and methods used to measure total carbon dioxide (TCO₂), total alkalinity (TALK), and pH at hydrographic stations during the R/V Hespérides oceanographic cruise in the Atlantic Ocean (Section A5). Conducted as part of the World Ocean Circulation Experiment (WOCE), the cruise began in Cadiz, Spain, on July 14, 1992, and ended in Miami, Florida, on August 15, 1992. Measurements made along WOCE Section A5 included CTD pressure, temperature, salinity, and oxygen; and bottle salinity, oxygen, phosphate, nitrate, nitrite, silicate, TCO₂, TALK, and pH.

The TALK, TCO₂, and pH were determined from titrations of seawater collected at 33 stations. The titration systems for measuring TALK and TCO₂ were calibrated in the laboratory with certified reference materials (CRMs) before the cruise to ensure traceable results. Standard reference seawater provided by Andrew Dickson of Scripps Institution of Oceanography (SIO) was used at sea to monitor the performance of the titration systems. The results agree with the laboratory results to ±2 μmol/kg for TALK and ±1 μmol/kg for TCO₂. The titration systems used to measure pH were calibrated with TRIS seawater buffers prepared in the laboratory and measured with an H₂, Pt/AgCl, Ag electrode. The initial electromotive force (emf) of the titrations was used to determine the pH. The values of pH are thought to be reliable to ±0.01 and are internally consistent with the measured values of TALK and TCO₂ to ±7 μmol/kg. The measured carbon dioxide system parameters have been used to calculate the in situ values of the fugacity of CO₂ (fCO₂) for the surface water. The surface results are briefly discussed.

WOCE section A5 is located at 24.5° N along the meridional overturn in the Atlantic Ocean. The maximum heat transfer in the North Atlantic Ocean occurs at 24° N; warming in the ocean at this latitude goes down to 3000 m. This section has been studied for a number of years and thus can be used to examine the changes that have occurred in the North Atlantic deep waters. This section has also been studied in the past using inverse methods to look at the movement of CO₂ to and from the North Atlantic.

The WOCE Section A5 hydrographic and carbonate data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center. The NDP consists of two oceanographic data files, two FORTRAN 77 programs, a documentation file, and this printed report, which describes the contents and format of all files as well as the procedures and methods used to obtain the data. Instructions on how to access the data are provided.

Keywords: Carbon dioxide; World Ocean Circulation Experiment; North Atlantic Ocean; hydrographic measurements; alkalinity; carbon cycle
PART 1:

OVERVIEW
1. BACKGROUND INFORMATION

There is currently much interest in understanding the inorganic carbon dioxide (CO$_2$) system in the oceans. This is due to the increasing atmospheric concentration of CO$_2$ enhancing the earth-atmosphere system's natural greenhouse effect and potentially affecting the earth's climate. Approximately 40% of the CO$_2$ added to the atmosphere as a result of the burning of fossil fuels is thought to be in turn absorbed into the oceans. The flux of carbon dioxide across the air-sea interface is controlled by the difference in the partial pressure of CO$_2$ in the atmosphere and in the surface waters. Once the CO$_2$ is in solution it can equilibrate with the bicarbonate and carbonate ions. The carbonate ion concentration in the oceans controls the rate of precipitation and dissolution of calcium carbonate (CaCO$_3$) in the oceans. The carbon dioxide system can be characterized by measuring two of the four measurable parameters (pH, the fugacity of CO$_2$ (fCO$_2$), the total carbon dioxide (TCO$_2$), and the total alkalinity (TALK)). The other parameters can be calculated using thermodynamic relations.

To learn more about the role of the world ocean in climate dynamics, several large ocean experiments have been conducted. The World Ocean Circulation Experiment (WOCE) is the largest such experiment ever attempted. A major component of the World Climate Research Program (WCRP), WOCE brings together scientists from more than 30 nations. Although TCO$_2$ is not an official WOCE measurement, carbonate chemists are participating in the WOCE cruises as part of the Joint Global Ocean Flux Study (JGOFS) to measure the components of the carbon dioxide system in the oceans. These studies are being sponsored in the United States by the U.S. Department of Energy (DOE) and the National Oceanographic and Atmospheric Administration (NOAA). The carbon dioxide system parameters measured, in order of preference, are the TCO$_2$, TALK, and pH. Preferred analytical methods are coulometry for TCO$_2$, titration for TALK, spectroscopy for pH, and infrared (IR) or gas chromatography (GC) for fCO$_2$. Because coulometry and IR or GC systems to measure TCO$_2$ and fCO$_2$, respectively, were not available on the R/V Hespérides cruise, and because only one berth was available, the TALK, TCO$_2$, and pH were determined by titration. Although this is not ideal, it was believed that some reasonably precise data were better than no data.

The present report gives the results of carbonate measurements made during the 32 days of the expedition of the R/V Hespérides along WOCE section AS (along 24.5° N) (Fig. 1).
Fig. 1. The cruise track during R/V Hespérides Cruise HE06 (WOCE Section A5).
2. DESCRIPTION OF THE EXPEDITION

2.1 R/V Hespérides Cruise Information

Ship name: R/V Hespérides
Expedition code: 29HE06/1
WOCE Section: A5
Location: Cadiz, Spain; to Santa Cruz de Tenerife, Canary Islands; to Las Palmas de Gran Canaria, Canary Islands; to Miami, Florida, U.S.A.
Dates: July 14 – August 15, 1992
Chief scientist: Gregorio Parrilla

Parameters measured | Institution | Principal Investigator
--- | --- | ---
CTD\(^1\) | IEO | G. Parrilla
 | WHOI | H. Bryden
Salinity | IEO | R. Molina
Oxygen | IEO | J. Escáñez
Nutrients | CEAB | A. Cruzado
Chlorofluorocarbons (CFCs) | LDEO | W. Smethie
pH, TALK, TCO\(_2\) | IIM | A. Rios
 | RSMAS | F. Millero
Calcium | IIM | G. Roson
Chlorophyll pigments | IEO | J. García Braun
 | CEAB | Z. Velazquez
Primary productivity | IEO | J. García Braun
Aluminum | FCMLP | J. Hernández
Radiocarbon (\(^{14}\)C) | LDEO | W. Broecker
ADCP\(^2\) | UPC | M. Garcia

Participating Institutions

CEAB       El Centro de Estudios Avanzados de Blanes
FCMLP      Facultad de Ciencias del Mar
IEO        Instituto Español de Oceanografía
IIM        Instituto de Investigaciones Marinas
LDEO       Lamont-Doherty Earth Observatory
RSMAS      Rosenstiel School of Marine and Atmospheric Science
UPC        Universidad Politecnica de Cataluña
WHOI       Woods Hole Oceanographic Institution

---
\(^1\)Conductivity, temperature, and depth sensor.
\(^2\)Acoustic Doppler current profiler.
2.2 Brief Cruise Summary

According to the WOCE Implementation Plan, the cruise line for WOCE Section A5 was to be located at 24° N. Since two oceanographic sections had previously been made (1957 and 1981) around 24.5° N (Roemmich and Wunsch 1985), the WOCE International Program Office (IPO) agreed to a request by the chief scientist to move WOCE Section A5 to this latitude for data comparison purposes.

The R/V Hespérides departed from Cadiz, Spain, on July 14, 1992. The cruise track and station locations are shown in Fig. 1. During the cruise, 118 CTD/rosette stations were occupied. Six stations were made to test the CTD and rosette. Four test stations were occupied before the ship arrived at Santa Cruz de Tenerife, Canary Islands, on July 17. The ship left Tenerife on July 18 and occupied two more test stations before arriving at Las Palmas de Gran Canaria. (The data from the six test stations are not included in this NDP.) The ship departed from Las Palmas in the early hours of July 20 and arrived at the first station of WOCE Section A5 the same day. After 101 stations were made, the ship arrived at the Bahamas on August 14 and WOCE Section A5 was completed. During the next day, 11 additional hydrographic stations were collected in the Straits of Florida and the cruise was concluded. For navigation and placement of stations, a global positioning system (GPS) was used.

Because of ship time constraints, station spacing was determined as follows: The first six stations of WOCE Section A5 were located at the 50-, 100-, 150-, 1500-, 2000-, and 2500-m isobaths and were about 18 nautical miles (nm) apart; from there to the 4000-m depth (Station 12), the distance between stations was about 23 nm. From Station 12 to the eastern limits of the Mid-Atlantic Ridge, the stations were separated by 36 nm. Across the Ridge, the separation was 32 nm. From the western limits of the Mid-Atlantic Ridge to the 5000-m isobath near the Bahamas, stations were again separated by 36 nm. Stations close to the Bahamas were separated by less than 30 nm. The stations across the Straits of Florida were occupied every 5 nm.

Near the Bahamas, the expedition deviated slightly from the planned cruise track in order to cross the continental slope perpendicularly to the direction of the isobaths and to obtain a clear crossing of the Deep Western Boundary Current.

The ADCP and a thermosalinograph recorded continuously during the entire cruise. Wind information was recorded every hour. Basic sampling equipment included three CTDs and a 24-bottle General Oceanics (GO) rosette system equipped with 10- or 12-L water sampling bottles.

The TCO₂ concentration was determined in 660 samples from 33 of the 112 CTD stations occupied during the cruise (Fig. 2).

At the end of the cruise the ship was checked for tritium and ¹⁴C contamination by the Tritium Laboratory of the University of Miami.
Fig. 2. Sampling depths at all hydrographic stations occupied during R/V Hespérides expedition along WOCE Section A5.
3. DESCRIPTION OF VARIABLES AND METHODS

3.1. Hydrographic Measurements

The *R/V Hesperides* carried three CTDs, two belonging to the Instituto Español de Oceanografía (IEO) and one belonging to Woods Hole Oceanographic Institution (WHOI). The two EG&G/NBIS Mark IIIb CTD underwater units belonging to IEO were each equipped with pressure, temperature, conductivity, and polygraphic oxygen sensors and were used throughout the cruise. Each CTD was configured identically with the same data scan length, variables, and scanning rate of 31.25 Hz. A detailed description of the Mark IIIb CTD can be found in Brown and Morrison (1978). Both instruments were modified at WHOI to add a titanium pressure sensor with a separately digitized resistive temperature device (RTD) (Millard et al. 1993). The third EG&G/NBIS Mark IIIb CTD was provided by WHOI but was not used during this expedition. A General Oceanics (GO) rosette fitted with 24 10- or 12-L Niskin bottles was used with the CTD for collecting water samples. The GO rosette bottles were mounted approximately 0.5 m above the CTD sensors. The conductivity and oxygen sensors were also calibrated at sea using the analysis of the water samples collected at each station. The depths of the sampling stations were based on classical standard depths, although they varied on a station by station basis according to participants' needs to sample a particular layer, provided there was no impairment of the in situ calibration activities. Because of delays inflicted by Hurricane Andrew on the equipment shipment from Miami to Woods Hole, the post-cruise calibrations were not performed on the CTD sensors until December.

All water sample measurements for bottle salinity and bottle oxygen were made in a constant temperature laboratory soon after each cast was completed. Water samples for salinity were collected from the Niskin bottles in Ocean Scientific International glass bottles, and the measurements were made within 24 hours after the station was finished. In total, 2,294 samples were measured. The bottle salinities were measured with a Guildline Autosal® Model 8400A salinometer. The manufacturer claims a precision of 0.0002 and an accuracy of 0.003 when the instrument is operated at a temperature between +4 and −2°C of ambient temperature. All salinity measurements were made in a temperature-controlled laboratory about 1–3°C below that of the salinometer water bath.

Bottle oxygen determinations were carried out following the Winkler method and using the reagents prepared according to Carpenter (1965). On this cruise, the modified Carpenter's equation as given by Culberson et al. (1991) was used. The endpoint of titration was determined visually using starch as the indicator. Reagents were dispensed with 0- to 2-ml capacity Dispensette® glass and teflon dispensers from BRAND GMBH & CO. The dispensers had a certified accuracy of ≤0.6% and a coefficient of variation of ≤0.1%. The tips of the dispensers were lengthened up to 6 cm with thin plastic tubing to avoid the precipitation of manganese hydroxide in the neck of sample flasks. Titration was done with a Metrohm Dosimat® E,412 automatic burette.

Samples for nutrient analyses (silicate, nitrate, nitrite, and phosphate) were collected in 150-mL acid-rinsed polythene flasks directly from the Niskin bottles, following the protocol established by the WOCE Hydrographic Program. Analyses were performed onboard with a four-channel Skalar, Inc. segmented flow autoanalyzer. Analyses were carried out immediately without any treatment of the samples. When necessary, samples were kept in the cold room (unfrozen and never for more than 10 hours) without additives. The analytical techniques followed were those described by Whittle et al. (1981) with minor modifications to adapt them to the particular conditions of the instrument used and concentration ranges observed. Primary standards were prepared at the beginning and in the middle of the cruise following Whittle et al. (1981). Secondary standards were prepared every two days and preserved
with several drops of chloroform in the refrigerator. Running standards of various concentrations were prepared daily, and calibration curves were run at the beginning of each session. Standards were interleaved with unknown samples in order to provide a measure of analytical stability. Whenever changes in sensitivity were noticed (particularly in the case of nitrate), the standards allowed for a correction to be applied. All concentrations were referred to double distilled water prepared by reverse osmosis. No seawater sample has ever given a concentration negative with respect to this double distilled water. Phosphate analyses were corrected for the change in absorbance as a result of the salinity effect. Surface seawater was used as a carrier and, except for silicate, it always showed the minimum concentrations in the water column. Silicate concentrations below the surface were often found to be lower than those at the surface and very close to the values given by double distilled water. Replicate samples were analyzed at various depths.

More detailed information on hydrographic measurements can be found at http://whpo.ucsd.edu/data/ontime/atlantic/a05/index.htm.

3.2 Carbon Measurements

The total alkalinity (TALK), total carbon dioxide (TCO₂), and pH were determined from titrations of seawater collected at 33 stations. The titration systems were calibrated with Dickson standard seawater before and during the cruise. The pH was determined from the initial emf reading relative to TRIS buffers. The results for Dickson samples agree with laboratory spectroscopic measurements for pH to ±0.005.

3.2.1 Methods for Measurement and Computation

Three titration systems (Thurmond and Millero 1982) were used to determine the TALK. Each system consisted of a Metrohm 655 Dosimat titrator and an Orion 720A pH meter that was operated by a personal computer (PC) (Millero et al. 1993a). The titration was made by adding HCl to the seawater past the carbonic acid end point (pH = 3.5). The solutions were contained in water-jacketed cells (230 cm³) controlled to a constant temperature of 25°C with a Forma temperature controller. The computer program used to perform the titration was developed in the Rosenstiel School of Marine and Atmospheric Science (RSMAS) laboratory using RS232 interfaces. A BASIC program was used to run the titration and record the volume of the added acid and the emf of the electrode system. A typical titration recorded the emf after the readings became stable (0.09 mV) and added enough acid to change the voltage to a preassigned value (13 mV). A full titration (25 points) took about 20 minutes. Using two systems, a 24-bottle cast could be analyzed in 4–5 hours.

The electrode systems used to measure the emf of the sample during a titration consisted of a ROSS glass pH electrode and an Orion double-junction reference electrode. A number of electrodes were screened to select those to be used in the titration systems. Electrodes with non-Nerstian behavior (slopes 1.0 mV different from theoretical) in acidic solutions were discarded. The reliability of a glass-reference electrode pair was determined by titrating 0.7-M NaCl solutions with HCl, by using seawater buffers (Ramette et al. 1977), and by determining the TALK of TCO₂ CRMs provided by Dr. Andrew Dickson of SIO. The titrations of 0.7-M NaCl solutions were used to evaluate the electrode slope in acidic solutions (pH = 2 and ≤ 4). Seawater buffers (Millero et al. 1993b) were used to evaluate the electrode slope near a pH of 8. The resulting experimental electrode slopes found for the cells used in the present study are given in Table 1. The slopes near a pH of 8 were lower than the theoretical value (59.16 mV), whereas the slopes near a pH of 3 were near the theoretical value. The electrodes were also evaluated by determining the TALK, TCO₂, and pH of TCO₂ CRMs. The results are
given in Table 2. The results indicate that precise values of TALK (±1.8 μmol/kg), TCO₂ (±5 μmol/kg), and pH (±0.005) can be obtained on weighed samples of seawater. The precision of the pH measurements for a given electrode (0.003) is better than the average deviation from the mean (0.005).

<table>
<thead>
<tr>
<th>Cell</th>
<th>Volume (cm³)</th>
<th>Electrode slope buffer calibration</th>
<th>Standard deviation</th>
<th>Electrode slope acid calibration</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>212.59</td>
<td>58.40</td>
<td>-0.80</td>
<td>59.00</td>
<td>-0.20</td>
</tr>
<tr>
<td>6.00</td>
<td>218.50</td>
<td>57.50</td>
<td>-1.70</td>
<td>59.60</td>
<td>0.40</td>
</tr>
<tr>
<td>7.00</td>
<td>234.29</td>
<td>58.00</td>
<td>-1.20</td>
<td>59.50</td>
<td>0.30</td>
</tr>
</tbody>
</table>

**Table 2. Titrations of certified reference materials (S = 33.82) in the laboratory**

<table>
<thead>
<tr>
<th>Seawater</th>
<th>TALK</th>
<th>TCO₂</th>
<th>pH</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch #12</td>
<td>2227.0 ± 1.8</td>
<td>2002.0 ± 5</td>
<td>7.930 ± 0.01</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.942 ± 0.0005&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Standard</td>
<td>2226.6</td>
<td>1984</td>
<td>7.940 ± 0.0002&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated from the initial emf using TRIS buffer calibration.

<sup>b</sup>From spectrophotometric measurements.

The HCl acid solutions used throughout the cruise were standardized in the laboratory. The approximately 0.25-M HCl solutions used contained 0.45-M NaCl to yield an ionic strength equivalent to average seawater (0.7 M). Approximately 20 liters of acid were made up in the laboratory. The calibrated acid was stored in 500 cm³ bottles for use at sea. The acid was standardized by titrating weighed amounts of Na₂CO₃ and TRIS dissolved in 0.7-M NaCl solution. The blanks in the 0.7-M NaCl solutions were determined by using coulometry and by titrations of the NaCl solutions with and without added Na₂CO₃ and TRIS. The TCO₂ in the blanks and carbonate solutions was measured daily by a UIC coulometer. The coulometer was calibrated using CO₂ gas loops and CRMs. The blanks of the titrations of TRIS were obtained by extrapolation to zero-added salt. The alkalinity blanks in the NaCl were generally about 14 ± 1 μM. The concentrations of the standard acids obtained from Na₂CO₃ and TRIS were in good agreement (Millero et al. 1993a).

The volumes of the cells used at sea were determined in the laboratory by weighing the cells filled with water. The density of water at the temperature of the measurements (25°C) was calculated from the international equation of state of seawater (Millero and Poisson 1981). The nominal volumes of all the cells was about 230 cm³ and the values were determined to ±0.03 cm³. The reliability of the volumes was assessed by comparing the values of TALK obtained for standard solutions with open and closed cells.

A FORTRAN computer program has been developed to calculate the CO₂ parameters (pH<sub>1c</sub>, emf, TALK, TCO₂, and pK<sub>1</sub>) in Na₂CO₃ and seawater solutions. These programs are patterned after those developed by Dickson (1984). This program requires an input of the
concentration of the acid, the volume of the cell, the salinity, the temperature of analysis, volume of added HCl ($V_{HCl}$), and the corresponding measured values of the emf. To obtain a reliable TALK from a full titration, at least 25 points have to be collected. The precision of the fit is less than 0.4 μmol/kg when $pK_1^*$ is allowed to vary, and 1.5 μmol/kg when $pK_1^*$ is fixed. This titration program has been compared with the titration programs used by others (Dickson 1981; C. Goyet, WHOI, personal communication, 1992; Bradshaw and Brewer 1988), and the values of TALK agree to within ±1 μmol/kg. Copies of the titration and calculation programs used are available upon request from Frank J. Millero (fmillero@rsmas.miami.edu).

### 3.2.2 Calibrations

Before the cruise, a number of titrations were made on CRMs (#12) in the laboratory. The laboratory titration results for TALK, TCO$_2$, and pH are given in Table 2 along with the assigned TCO$_2$ and the pH measured relative to TRIS buffers (Dickson 1993) and spectrophotometrically (Byrne and Breiland 1989; Robert-Baldo et al. 1985; Millero et al. 1993b; Clayton and Byrne 1993). It should be pointed out that the values of pH are on the seawater scale defined by Dickson (1984):

$$\text{pH}_{sws} = -\log[H^+]_{sws} = -\log([H^+] + [HSO_4^-] + [HF])$$

(1)

The precision in the values of TALK (±2 μmol/kg), TCO$_2$ (±5 μmol/kg), and pH (±0.005) was quite good. The titration values of TCO$_2$ were $18 \pm 4$ μmol/kg higher than the values assigned and measured by coulometry. The titration values of pH ($7.93 \pm 0.01$) were 0.01 lower than the values measured by spectrophotometric methods ($7.940 \pm 0.002$) and using seawater buffers (Millero et al. 1993b). The differences in pH and TCO$_2$ are caused by the non-ideal behavior of the electrodes near a pH of 8 (Millero et al. 1993a). Calibration of the electrodes using TRIS seawater buffers yielded a pH of 7.942 ± 0.005 from the initial emf readings of the titration. These results are in excellent agreement with the spectrophotometrically determined pH and show a lower standard error than the values determined from the titrations.

The program used to calculate the TCO$_2$ parameters assumed that the electrodes would respond to a change in pH with an ideal slope of 59.2 mV at 25°C as determined from the Nernst equation. The slopes of the electrodes using buffers and titrating with HCl frequently gave non-ideal behavior. The parameters produced by varying this slope indicated (Millero et al. 1993a) that the deviations resulting from these changes were much greater for TCO$_2$ than for TALK. Errors of 1.0 mV in the slope yielded differences in TALK and TCO$_2$, respectively, of 2.1 and 22.8 μmol/kg when the $pK_1^*$ was also allowed to vary (Millero et al. 1993a). The values of TALK were not strongly affected by the behavior of the electrodes. The values of TCO$_2$ and pH determined for the CRMs with the buffer-derived slope (58.4) were in good agreement with the correct values (pH = 7.935 and TCO$_2$ = 1984 μmol/kg). These calculations indicated that the deviations in the TCO$_2$ derived from titration were a result of errors in the slope of the electrode, and not a result of unknown protolites (Bradshaw and Brewer 1988). If the slope determined from the buffers was used, the titrations yielded reliable values of pH, TALK and TCO$_2$. This fact was used to make sure that the field titration measurements yielded the most reliable values of pH and TCO$_2$.

During the cruise, the electrodes in each titration system were calibrated with TRIS seawater buffers (Millero 1986) of known pH$_{sws}$ (8.057) determined with a H$_2$, Pt/AgCl, Ag electrode (Millero et al. 1993b). Titrations of CRMs (#12) were also made during the cruise. The results are given in Table 3. The average values, TALK = 2229 ± 7 μmol/kg, TCO$_2$ = 1984 ± 6 μmol/kg, and pH = 7.944 ± 0.01, are in good agreement with the laboratory.
results. The deviations are larger at sea than obtained in the laboratory (Table 2) but indicate that the titration systems performed well throughout the cruise. The large errors are related to problems in reproducing the volume in the glass cells. Presently, a plastic cell with a more reproducible volume is used, making it possible to reproduce the CRMs to $\pm 2 \mu$mol/kg for TALK, to $\pm 3 \mu$mol/kg for TCO$_2$, and to $\pm 0.005$ for pH (Millero et al. 1993a).

<table>
<thead>
<tr>
<th>Cell</th>
<th>TALK</th>
<th>TCO$_2$</th>
<th>pH</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2229 $\pm$ 6</td>
<td>1983 $\pm$ 5</td>
<td>7.937 $\pm$ 0.009$^a$</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>2230 $\pm$ 8</td>
<td>1981 $\pm$ 8</td>
<td>7.944 $\pm$ 0.021$^a$</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>2229 $\pm$ 6</td>
<td>1984 $\pm$ 8</td>
<td>7.948 $\pm$ 0.013$^a$</td>
<td>12</td>
</tr>
<tr>
<td>Average</td>
<td>2229 $\pm$ 7</td>
<td>1984</td>
<td>7.942 $\pm$ 0.014</td>
<td>31</td>
</tr>
<tr>
<td>Standard</td>
<td>2226.6$^b$</td>
<td>1984$^c$</td>
<td>7.940$^d$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Calculated from the initial cmf using TRIS buffer calibration.
$^b$Certified value from weighted titrations.
$^c$Certified value from manometric extraction technique.
$^d$Results obtained in the laboratory using spectrophotometric methods.

### 3.2.3 Results

The cruise track of the R/V Hesperides is shown in Fig. 1. A summary of the 33 TCO$_2$ stations that were sampled during the cruise is given in Table 4. Based upon the CRM calibrations at sea, the accuracy of the measured parameters is estimated to be $\pm 7 \mu$mol/kg for TALK and TCO$_2$ and $\pm 0.02$ for pH. The thermodynamic consistency of the measurements can be shown by comparing the calculated values of pH (7.944), TALK (2334 $\mu$mol/kg), and TCO$_2$ (1984 $\mu$mol/kg) using the constants of Roy et al. (1993) with the measured values (Table 3). The agreement is quite good. The values of TALK, TCO$_2$, and pH as a function of depth for all of the samples are shown in Figs. 3–5. Plots of the surface properties of the waters sampled are shown in Figs. 6–8.

The temperature increases from 22°C near the Spanish coast to 27°C off the coast of Florida. The salinities go through a maximum (37.5) between stations 20 to 50 (30° to 45° W). The surface values of TALK (Fig. 7) follow this trend. The TCO$_2$ is fairly constant from stations 1 to 60 (2108 ± 10 $\mu$mol/kg) and decreases off the coast of Florida to 2020 $\mu$mol/kg. The pH at 25°C increases from 8.05 off the coast of Spain to about 8.12 off the coast of Florida (average pH = 8.05 ± 0.03). The values of TALK and TCO$_2$ normalized to S = 35 are shown in Fig. 8. The average normalized TALK is 2293 ± 4 $\mu$mol/kg for the surface waters, whereas the average normalized TCO$_2$ is 1970 ± 20 $\mu$mol/kg. The in situ fugacities of CO$_2$ ($f$CO$_2$) calculated from the measured values of TALK and TCO$_2$ are shown in Fig. 8. From these calculations, the surface waters ($f$CO$_2$ = 402 ± 15 μatm) are supersaturated with CO$_2$ ($\Delta f$CO$_2$ = 42 ± 15 μatm) for all the surface waters.
Table 4. Summary of carbonate system stations occupied during the cruise

<table>
<thead>
<tr>
<th>Station no.</th>
<th>Latitude  (^{\circ})N</th>
<th>Longitude  (^{\circ})W</th>
<th>Depth (m)</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24°29'</td>
<td>15°58'</td>
<td>53</td>
<td>7/20/1992</td>
</tr>
<tr>
<td>3</td>
<td>24°29'</td>
<td>16°29'</td>
<td>575</td>
<td>7/20/1992</td>
</tr>
<tr>
<td>8</td>
<td>24°29'</td>
<td>18°20'</td>
<td>2736</td>
<td>7/20/1992</td>
</tr>
<tr>
<td>11</td>
<td>24°30'</td>
<td>19°35'</td>
<td>3393</td>
<td>7/22/1992</td>
</tr>
<tr>
<td>13</td>
<td>24°30'</td>
<td>20°40'</td>
<td>4186</td>
<td>7/23/1992</td>
</tr>
<tr>
<td>15</td>
<td>24°30'</td>
<td>21°59'</td>
<td>4705</td>
<td>7/24/1992</td>
</tr>
<tr>
<td>18</td>
<td>24°30'</td>
<td>23°59'</td>
<td>5149</td>
<td>7/24/1992</td>
</tr>
<tr>
<td>21</td>
<td>24°30'</td>
<td>25°59'</td>
<td>5403</td>
<td>7/25/1992</td>
</tr>
<tr>
<td>25</td>
<td>24°30'</td>
<td>28°39'</td>
<td>5723</td>
<td>7/26/1992</td>
</tr>
<tr>
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<td>30°38'</td>
<td>5745</td>
<td>7/27/1992</td>
</tr>
<tr>
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<td>32°40'</td>
<td>6426</td>
<td>7/28/1992</td>
</tr>
<tr>
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<td>34°40'</td>
<td>5354</td>
<td>7/29/1992</td>
</tr>
<tr>
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<td>5008</td>
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</tr>
<tr>
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<td>4580</td>
<td>7/30/1992</td>
</tr>
<tr>
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<td>40°35'</td>
<td>4551</td>
<td>7/31/1992</td>
</tr>
<tr>
<td>46</td>
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<td>4430</td>
<td>8/01/1992</td>
</tr>
<tr>
<td>49</td>
<td>24°30'</td>
<td>44°04'</td>
<td>4182</td>
<td>8/01/1992</td>
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<tr>
<td>60</td>
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<td>8/04/1992</td>
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<td>51°39'</td>
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<td>8/04/1992</td>
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<tr>
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<td>8/05/1992</td>
</tr>
<tr>
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<td>54°40'</td>
<td>6275</td>
<td>8/05/1992</td>
</tr>
<tr>
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<td>24°30'</td>
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<td>6024</td>
<td>8/06/1992</td>
</tr>
<tr>
<td>73</td>
<td>24°30'</td>
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<td>8/07/1992</td>
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<tr>
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<td>5965</td>
<td>8/08/1992</td>
</tr>
<tr>
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<td>5858</td>
<td>8/09/1992</td>
</tr>
<tr>
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<td>65°59'</td>
<td>5832</td>
<td>8/10/1992</td>
</tr>
<tr>
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<td>24°30'</td>
<td>68°00'</td>
<td>5805</td>
<td>8/11/1992</td>
</tr>
<tr>
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<td>70°00'</td>
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</tr>
<tr>
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<td>24°30'</td>
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<td>5571</td>
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</tr>
<tr>
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<td>25°00'</td>
<td>74°20'</td>
<td>4994</td>
<td>8/13/1992</td>
</tr>
<tr>
<td>101</td>
<td>24°30'</td>
<td>75°31'</td>
<td>1040</td>
<td>8/14/1992</td>
</tr>
</tbody>
</table>
Fig. 4. Measured values of total alkalinity (TALK) vs depth for all stations.
Fig. 5. Measured values of total carbon dioxide (TCO$_2$) vs depth for all stations.
Fig. 6. Surface salinity and temperature vs station number.
Fig. 7. Surface total alkalinity (TALK), total carbon dioxide (TCO₂), and pH vs station number.
Fig. 8. Surface values of normalized TALK and TCO$_2$, pH at 25°C, and calculated fugacity of CO$_2$ (fCO$_2$) vs station number.
4. DATA CHECKS AND PROCESSING PERFORMED BY CDIAC

An important part of the NDP process at the Carbon Dioxide Information Analysis Center (CDIAC) involves the quality assurance (QA) of data before distribution. Data received at CDIAC are rarely in a condition that would permit immediate distribution, regardless of the source. To guarantee data of the highest possible quality, CDIAC conducts extensive QA reviews that involve examining the data for completeness, reasonableness, and accuracy. The QA process is a critical component in the value-added concept of supplying accurate, usable data for researchers.

The following information summarizes the data processing and QA checks performed by CDIAC on the carbon-related, hydrographic, and chemical data obtained during the R/V *Hesperides* cruise along WOCE Section A5 in the Atlantic Ocean.

1. Carbon-related data and hydrographic measurements were provided to CDIAC by Frank Millero (RSMAS). The final hydrographic and chemical measurements and the station information files were provided by the WOCE Hydrographic Program Office (WHPO) after quality evaluation. A FORTRAN 77 retrieval code was written and used to merge and reformat all data files.

2. To check for obvious outliers, all data were plotted using a PLOTNEST.C program written by Stewart C. Sutherland (Lamont-Doherty Earth Observatory). The program plots a series of nested profiles, using the station number as an offset; the first station is defined at the beginning, and subsequent stations are offset by a fixed interval (Figs. 9–11). Several outliers were identified and marked with the quality flags of “3” (questionable measurement) or “4” (bad measurement) (see File Descriptions in Section 7 of this documentation).

3. To identify “noisy” data and possible systematic, methodological errors, property-property plots for all parameters were generated (Fig. 12), carefully examined, and compared with plots from previous expeditions in the Atlantic Ocean.

4. All variables were checked for values exceeding physical limits, such as sampling depth values greater than the given bottom depths.

5. Dates, times, and coordinates were checked for bogus values (e.g., values of MONTH < 1 or > 12; DAY < 1 or > 31; YEAR < or > 1992; TIME < 0000 or > 2400; LAT < 20.000 or > 30.000; and LONG < -90.000 or > 0.000).

6. Station locations (latitudes and longitudes) and sampling times were examined for consistency with maps and cruise information supplied by Frank J. Millero of RSMAS.

7. The designation for missing values, given as -9.0 in the original files, was changed to -999.9 for consistency with other oceanographic datasets.
Fig. 9. Nested profiles: Total carbon dioxide ($\mu$mol/kg) vs pressure (dbar) for all stations of WOCE Section A5.
WOCE Section A5
Total Alkalinity (all stations)
Only profiles which exist in this Pressure (dbar) range are plotted.
Plotted parameter ranges from 2300 to 2500

Fig. 10. Nested profiles: Total alkalinity (μmol/kg) vs pressure (dbar) for all stations of WOCE Section A5.
WOCE Section A5
pH (all stations)

Only profiles which exist in this Pressure (dbar) range are plotted.
Plotted parameter ranges from 7.4 to 8.2

Fig. 11. Nested profiles: pH vs pressure (dbar) for all stations of WOCE Section A5.
Fig. 12. Property-property plots for all stations occupied during R/V Hespérides Cruise HE06 (WOCE Section A5).
5. HOW TO OBTAIN THE DATA AND DOCUMENTATION

This database (NDP-074) is available free of charge from CDIAC. The complete documentation and data can be obtained from the CDIAC oceanographic Web site (http://cdiac.esd.ornl.gov/oceans/doc.html), through CDIAC's online ordering system (http://cdiac.esd.ornl.gov/pns/how_order.html), or by contacting CDIAC.

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

    ftp cdiac.esd.ornl.gov or >ftp 128.219.24.36
    Login: "anonymous" or "ftp"
    Password: your e-mail address
    ftp> cd pub/nep074/
    ftp> dir
    ftp> mget (files)
    ftp> quit

Contact information:

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

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

    E-mail: cdiac@ornl.gov

    Internet: http://cdiac.esd.ornl.gov/
6. REFERENCES


Dickson, A. G. 1984. pH scales and proton-transfer reactions in saline media such as seawater. Geochemica et Cosmochemica Acta 48:2299–2308.


PART 2:

CONTENT AND FORMAT OF DATA FILES
7. FILE DESCRIPTIONS

This section describes the content and format of each of the five files that comprise this NDP (see Table 5). Because CDIAC distributes the data set in several ways, (e.g., via anonymous FTP and on floppy diskette), each of the five files is referenced by both an ASCII file name, which is given in lowercase, bold-faced type (e.g., ndp074.txt) and a file number. The remainder of this section describes (or lists, where appropriate) the contents of each file.

Table 5. Content, size, and format of data files

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<thead>
<tr>
<th>File number, name, and description</th>
<th>Logical records</th>
<th>File size in bytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ndp074.txt:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a detailed description of the cruise, listings of the two provided FORTRAN 77 programs, and descriptions of the content and format of the two oceanographic files.</td>
<td>1,144</td>
<td>57,492</td>
</tr>
<tr>
<td>2. stainv.for:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a FORTRAN 77 program to read and print a5sta.dat (file 4)</td>
<td>44</td>
<td>1,331</td>
</tr>
<tr>
<td>3. a5dat.for:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a FORTRAN 77 program to read and print a5.dat (file 5)</td>
<td>53</td>
<td>2,070</td>
</tr>
<tr>
<td>4. a5sta.dat:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a listing of the station locations, sampling dates, and sounding bottom depths for each of the 112 stations of WOCE Section A5.</td>
<td>123</td>
<td>9,593</td>
</tr>
<tr>
<td>5. a5.dat:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrographic, carbon dioxide, and chemical data from the 112 stations occupied on WOCE Section A5.</td>
<td>2,487</td>
<td>401,604</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3,851</strong></td>
<td><strong>472,090</strong></td>
<td></td>
</tr>
</tbody>
</table>

7.1 ndp074.txt (File 1)

This file contains a detailed description of the data set, listings of the two FORTRAN 77 programs used to read and print the data, and descriptions of the content and format of the two oceanographic data files. This file exists primarily for the benefit of individuals who acquire this database as machine-readable data files from CDIAC.

7.2 stainv.for (File 2)

This file contains a FORTRAN 77 program to read and print a5sta.dat (File 4). The following is a listing of this program. For additional information regarding variable definitions,
variable lengths, variable types, units, and codes, please see the description for a5sta.dat in Sect. 7.4.

c***********************************************************************
c* This is a Fortran 77 retrieval code to read and format the   *
c* station inventory file named a5sta.dat (File 4).            *
c***********************************************************************
c* Defines variables*
   INTEGER stat, cast, depth
   REAL latdcm, londcm
   CHARACTER expo*8, sect*3, date*10, time*4
   OPEN (unit=1, file='a5sta.dat')
   OPEN (unit=2, file='a5stat.dat')
   write (2, 5)

5    format (4X, 'STATION INVENTORY: R/V HESPERIDES, WOCE A5',/,
       1 'A3', 'EXPCODE', '1X', 'SECT', '1X', 'STNBR', '2X', 'CAST',
       2 '9X', 'DATE', '2X', 'TIME', '3X', 'LATITUDE', '3X', 'LONGITUDE', '2X,'
       3 'DEPT','/)

c* Writes out column labels*
   c* Sets up a loop to read and format all the data in the file*
   read (1, 6)
6    format (///////////)
   CONTINUE
   read (1, 10, end=999) expo, sect, stat, cast, date, time,
      latdcm, londcm, depth
   10   format (A12, 2X, A3, 3X, I3, 5X, I1, 3X, A10, 2X, A4, 4X,
      1 F7.3, 4X, F8.3, 3X, I4)
       write (2, 20) expo, sect, stat, cast, date, time,
      latdcm, londcm, depth
   20   format (A12, 2X, A3, 3X, I3, 5X, I1, 3X, A10, 2X, A4, 4X,
      1 F7.3, 4X, F8.3, 3X, I4)
   GOTO 7
   999  close(unit=5)
   close(unit=2)
   stop
end

7.3 a5dat.for (File 3)

This file contains a FORTRAN 77 program to read and print a5.dat (File 5). The following is a listing of this program. For additional information regarding variable definitions, variable lengths, variable types, units, and codes, please see the description for a5.dat in Sect. 7.5.

c***********************************************************************
c* FORTRAN 77 data retrieval routine to read and print the   *
c* file named "a5.dat" (File 5).                           *
c***********************************************************************
   CHARACTER qual*12
   INTEGER sta, cast, samp, bot
   REAL pre, ctdtmp, ctdsal, ctdoxy, theta, sal, oxy, silca
REAL nitrat, nitrit, phsplt, talk, tcarb, ph
OPEN (unit=1, file='a5.dat')

OPEN (unit=2, file='a5data.dat')
write (2, 5)

* Writes out column labels *
5      format (2X, 'STNNBR', 2X, 'CASTNO', 2X, 'SAMPNO', 2X, 'BTLNBR', 2X,
1      'CTDPRS', 2X, 'CTDTEMP', 2X, 'CTDSAL', 3X, 'CTDOXY', 3X, 'THETA', 4X,
2      'SALNTY', 2X, 'OXYGEN', 2X, 'SILCAT', 2X, 'NITRAT', 2X, 'NITRIT', 2X,
6      4X, 'PSS-78', 1X, 'UMOL/KG', 1X, 6('UMOL/KG', 1X), 1X, 'Q25_Deg', 12X,
8      '\*', '/', 25X, '******', 17X, 2('******', 2X), 9X, '******', 1X,
8      7('******', 1X), 1X, '******', 12X, '****')

* Sets up a loop to read and format all the data in the file *
6      read (1, 6)
6      format (1, 6)
7      CONTINUE
7      read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
7      ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
7      phsplt, talk, tcarb, ph, qualt
10     format (5X, I3, 7X, I1, 6X, I2, 6X, I2, 1X, F7.1, 1X, F7.4,
1      1X, F7.4, 1X, F8.3, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2,
2      1X, F7.2, 1X, F7.2, 1X, F7.2, 1X, F7.1, 1X, F7.1, 1X, F8.3,
3      1X, A12)

7      write (2, 20) sta, cast, samp, bot, pre, ctdtmp,
7      ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
7      phsplt, talk, tcarb, ph, qualt
20     format (5X, I3, 7X, I1, 6X, I2, 6X, I2, 1X, F7.1, 1X, F7.4,
1      1X, F7.4, 1X, F8.3, 1X, F7.4, 1X, F9.4, 1X, F7.1, 1X, F7.2,
2      1X, F7.2, 1X, F7.2, 1X, F7.2, 1X, F7.1, 1X, F7.1, 1X, F8.3,
3      1X, A12)
7      GOTO 7
999    close(unit=1)
7      close(unit=2)
7      stop
end

7.4 a5sta.dat (File 4)

This file provides station inventory information for each of the 112 stations occupied during the RV Hespérides cruise along WOCE Section A5. Each line of the file contains an expocode (expedition code unique to each cruise), section number, station number, cast number, sampling date (month/day/year), sampling time, latitude, longitude, and sounding depth. The file is sorted by station number and can be read by using the following FORTRAN 77 code (contained in stainv.for, File 2):

```
INTEGER stat, cast, depth
REAL latdcm, londcm
CHARACTER expo*8, sect*3, date*10, time*4
read (1, 10, end=999) expo, sect, stat, cast, date, time,
```

33
Stated in tabular form, the contents include the following:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Variable type</th>
<th>Variable width</th>
<th>Starting column</th>
<th>Ending column</th>
</tr>
</thead>
<tbody>
<tr>
<td>expo</td>
<td>Character</td>
<td>12</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>sect</td>
<td>Character</td>
<td>3</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>stat</td>
<td>Numeric</td>
<td>3</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>cast</td>
<td>Numeric</td>
<td>1</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>date</td>
<td>Character</td>
<td>10</td>
<td>33</td>
<td>42</td>
</tr>
<tr>
<td>time</td>
<td>Character</td>
<td>4</td>
<td>45</td>
<td>48</td>
</tr>
<tr>
<td>latdcm</td>
<td>Numeric</td>
<td>7</td>
<td>53</td>
<td>59</td>
</tr>
<tr>
<td>londcm</td>
<td>Numeric</td>
<td>8</td>
<td>64</td>
<td>71</td>
</tr>
<tr>
<td>depth</td>
<td>Numeric</td>
<td>4</td>
<td>75</td>
<td>78</td>
</tr>
</tbody>
</table>

The variables are defined as follows:

**expo** is the unique expedition code of the cruise;

**sect** is the WOCE section number;

**stat** is the station number;

**cast** is the cast number;

**date** is the sampling date (month/day/year);

**time** is the sampling time [Greenwich mean time (GMT)];

**latdcm** is the latitude of the station (in decimal degrees; negative values indicate the Southern Hemisphere);

**londcm** is the longitude of the station (in decimal degrees; negative values indicate the Western Hemisphere);

**depth** is the sounding depth of the station (in meters).
7.5 a5.dat (File 5)

This file provides hydrographic, carbon dioxide, and chemical data for the 112 stations occupied during the R/V Hespérides cruise along WOCE Section A5. Each line consists of a station number, cast number, sample number, bottle number, CTD pressure, CTD temperature, CTD salinity, CTD oxygen, potential temperature, bottle salinity, oxygen, silicate, nitrate, nitrite, phosphate, total alkalinity, total CO₂, pH at 25°C, and data-quality flags. The file is sorted by station number and pressure and can be read by using the following FORTRAN 77 code (contained in a5dat.for, File 3):

```
CHARACTER qual*12
INTEGER sta, cast, samp, bot
REAL pre, ctdtmp, ctdsal, ctdoxy, theta, sal, oxy, silca
REAL nitrat, nitrit, phsph, talk, tcarb, ph

read (1, 10, end=999) sta, cast, samp, bot, pre, ctdtmp,
1 ctdsal, ctdoxy, theta, sal, oxy, silca, nitrat, nitrit,
2 phsph, talk, tcarb, ph, qual
```

Stated in tabular form, the contents include the following:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Variable type</th>
<th>Variable width</th>
<th>Starting column</th>
<th>Ending column</th>
</tr>
</thead>
<tbody>
<tr>
<td>sta</td>
<td>Numeric</td>
<td>3</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>cast</td>
<td>Numeric</td>
<td>1</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>samp</td>
<td>Numeric</td>
<td>2</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>bot</td>
<td>Numeric</td>
<td>2</td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>pre</td>
<td>Numeric</td>
<td>7</td>
<td>34</td>
<td>40</td>
</tr>
<tr>
<td>ctdtmp</td>
<td>Numeric</td>
<td>7</td>
<td>42</td>
<td>48</td>
</tr>
<tr>
<td>ctdsal</td>
<td>Numeric</td>
<td>7</td>
<td>50</td>
<td>56</td>
</tr>
<tr>
<td>ctdoxy</td>
<td>Numeric</td>
<td>8</td>
<td>58</td>
<td>65</td>
</tr>
<tr>
<td>theta</td>
<td>Numeric</td>
<td>7</td>
<td>67</td>
<td>73</td>
</tr>
<tr>
<td>sal</td>
<td>Numeric</td>
<td>9</td>
<td>75</td>
<td>83</td>
</tr>
<tr>
<td>oxy</td>
<td>Numeric</td>
<td>7</td>
<td>85</td>
<td>91</td>
</tr>
<tr>
<td>silca</td>
<td>Numeric</td>
<td>7</td>
<td>93</td>
<td>99</td>
</tr>
<tr>
<td>nitrat</td>
<td>Numeric</td>
<td>7</td>
<td>101</td>
<td>107</td>
</tr>
<tr>
<td>nitrit</td>
<td>Numeric</td>
<td>7</td>
<td>109</td>
<td>115</td>
</tr>
<tr>
<td>Variable</td>
<td>Variable type</td>
<td>Variable width</td>
<td>Starting column</td>
<td>Ending column</td>
</tr>
<tr>
<td>------------</td>
<td>---------------</td>
<td>----------------</td>
<td>-----------------</td>
<td>---------------</td>
</tr>
<tr>
<td>phspht</td>
<td>Numeric</td>
<td>7</td>
<td>117</td>
<td>123</td>
</tr>
<tr>
<td>talk</td>
<td>Numeric</td>
<td>7</td>
<td>125</td>
<td>131</td>
</tr>
<tr>
<td>tcarb</td>
<td>Numeric</td>
<td>7</td>
<td>133</td>
<td>139</td>
</tr>
<tr>
<td>ph</td>
<td>Numeric</td>
<td>8</td>
<td>141</td>
<td>148</td>
</tr>
<tr>
<td>qualt</td>
<td>Character</td>
<td>12</td>
<td>150</td>
<td>161</td>
</tr>
</tbody>
</table>

The variables are defined as follows:

- **sta** is the station number;
- **cast** is the cast number;
- **samp** is the sample number;
- **bot** is the bottle number;
- **pre** is the CTD pressure (dbar);
- **ctdtmp** is the CTD temperature (°C);
- **ctdsal** is the CTD salinity [on the Practical Salinity Scale (PSS)];
- **ctdoxy** is the CTD oxygen (μmol/kg);
- **theta** is the potential temperature (°C);
- **sal** is the bottle salinity (on the PSS);
- **oxy** is the oxygen concentration (μmol/kg);
- **silca** is the silicate concentration (μmol/kg);
- **nitrat** is the nitrate concentration (μmol/kg);
- **nitrit** is the nitrite concentration (μmol/kg);
- **phspht** is the phosphate concentration (μmol/kg);
- **talk** is the total alkalinity concentration (μmol/kg);
- **tcarb** is the total carbon dioxide concentration (μmol/kg);
- **pH** is the pH at 25°C;
**qual** is a 12-digit character variable that contains data-quality flag codes for parameters underlined with asterisks (*****') in the file header.

Variables that are underlined with asterisks in the data file's header indicate they have a data-quality flag. Data-quality flags are defined as follows:

1 = sample for this measurement was drawn from water bottle but analysis was not received;
2 = acceptable measurement;
3 = questionable measurement;
4 = bad measurement;
5 = not reported;
6 = mean of replicate measurements;
7 = manual chromatographic peak measurement;
8 = irregular digital chromatographic peak integration;
9 = sample not drawn for this measurement from this bottle.