

S.I.O. REFERENCE SERIES

Oceanic CO₂ Measurements for the WOCE
Hydrographic Survey in the Pacific Ocean:
Shipboard Alkalinity Measurements on
CGC92 Legs 1 and 2, 1992

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1. Cruise Summary

Shipboard measurements of CO₂ system parameters in sea water were made on the Climate and Global Change 92 (CGC92) cruise of the Pacific Marine Environmental Laboratory (PMEL) of the National Oceanic and Atmospheric Administration (NOAA). The ship used for the cruise was the R/V *John Vickers* of the University of Southern California. The Chief Scientists were Dr. John Bulister on Leg 1 and Dr. Bruce Taft on Leg 2. Both are staff scientists at PMEL. The cruise, along approximately 165° E longitude between Dutch Harbor, Alaska and Noumea, New Caledonia, was designated Line P13 of the one - time survey of the World Ocean Circulation Experiment (WOCE). CO₂ system measurements on this cruise were carried out by the Carbon Dioxide Research Group (CDRG) of Scripps Institution of Oceanography (SIO) (Dr. Charles Keeling, Principal Investigator), with the assistance of Battelle NW Laboratory and of Dr. Andrew Dickson of SIO. Dr. Dickson and his group were responsible for measurements of Total Dissolved Inorganic Carbon (DIC) with a SOMMA coulometric titrator. The DIC analysts on Leg 1 were Mr. George Anderson of SIO and Mr. Ronald Citterman of Battelle NW and on Leg 2, Ms. Lori Bell of SIO and Mr. Citterman. The CDRG of SIO was responsible for measurements of Titration (or "Total") Alkalinity (ALK) with a potentiometric acid titration system. The ALK analysts on Leg 1 were Mr. Peter Guenther and Mr. Guy Emanuele, both of SIO, and on Leg 2, Dr. Andrew Dickson of SIO and Mr. Emanuele.

This report concerns only the ALK data. Dr. Dickson reports the DIC data in a separate report.

2. Shipboard Water Sampling Program

Samples for shipboard analysis of DIC and ALK were collected from 10 liter Niskin bottles on the 36 position small volume rosette water sampling system. Of the total of 84 stations on the two legs, CO₂ samples were collected from all Niskins throughout the water column on 39 stations (nominally 36 Niskins, but fewer depths were sampled on a number of stations). On an additional 41 stations CO₂ samples were collected from surface Niskins only. Stations sampled were located along about 165° E longitude between 54° N and 5° S latitude.

Samples were collected by established procedures (DOE,1994) in 500 ml borosilicate glass bottles equipped with greased ground glass joints held closed with rubber bands. Single samples were collected from most Niskins. On stations where CO₂ samples were collected throughout the water column, duplicate

samples were collected from two Niskins, one near the surface and one near the bottom, for quality assessment purposes. All samples were collected by the CO₂ analysts. Two persons worked as a team during sample collection. One analyst filled the bottles from the Niskins and the other adjusted the water volume, added the mercuric chloride poison and prepared and sealed the bottle joints. Additionally, replicate samples for shore based analyses of DIC and ALK were collected in duplicate from 161 Niskins on 34 stations.

Analyses of DIC and ALK were performed on aliquots of water subsampled from the same bottle of water. Single aliquots for DIC analysis were removed from the bottles first. Aliquots for ALK analysis were later removed from the same bottles. Enough water was available to perform at least two ALK titrations on each bottle.

3. Alkalinity Measurement Summary

Samples from a total of 1153 Niskins, 574 from Leg 1 and 579 from Leg 2, were titrated to determine ALK. Usually all 36 samples collected on a station were analyzed for ALK. A total of 72 duplicate samples, 36 on each leg, were also analyzed. For quality assessment purposes, 84 titrations were performed on 68 bottles of the natural sea water Certified DIC Reference Material Batch No. 13 and 182 more titrations were performed on 38 bottles of bicarbonate reference material solutions prepared at SIO. A total of 1636 individual titrations were performed during 44 days on the cruise, including all multiple trials on individual bottles of sea water and quality assessment samples.

4. Description of Analytical System and Procedures

4.1 Overall system description

The closed cell potentiometric acid titration system was designed and constructed at SIO by David Moss with the developmental and experimental assistance of Timothy Lueker. Figure 1 is a schematic diagram of the analytical system. It differs from other alkalinity titration systems in the method employed to define the volume of seawater to be titrated. This was accomplished by dispensing simultaneously constant volumes of water from two syringes into two titration cells so that two titrations could be run at the same time. Between titrations the cells were rinsed with purified water to remove all traces of acid or alkalinity from the cell. The cell volumes, after filling with water, were adjusted using a bladder to minimize the air space. This scheme eliminated the need to determine and

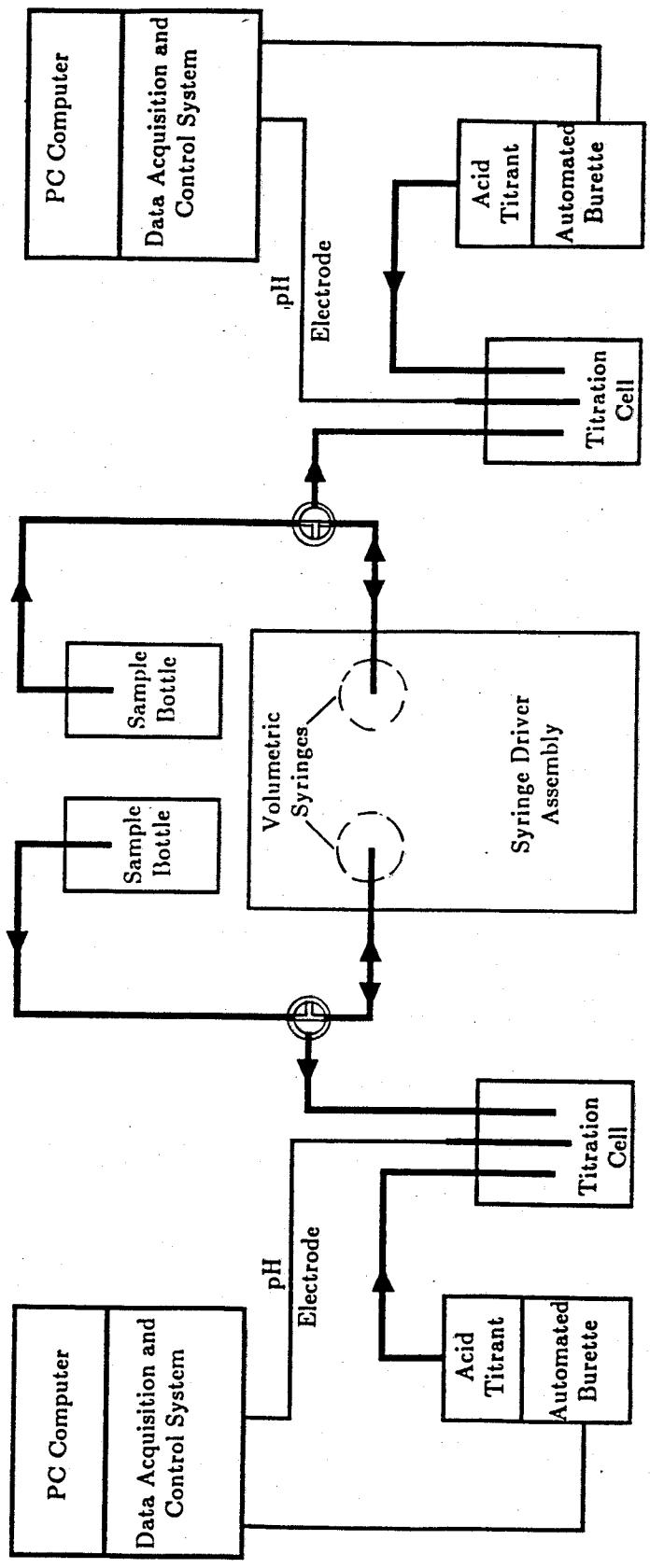


Figure 1. Schematic Diagram of the Dual Volumetric Alkalinity Titrator

control the cell volume. It added the requirement of calibrating and controlling the delivery of constant volumes by the syringe system. Calibration of the syringes was readily monitored at sea by delivering samples into pre - weighed septum bottles for later weighing at the shore laboratory.

The analytical system was modified in several ways after the TUNES Leg 3 cruise in 1991. Surface thermistor probes were attached to the outside surfaces of the glass syringes for measurement of the temperatures of the volumetric aliquots. A different type of glass electrode was used, and it was electrically shielded with a copper sleeve and a coaxial cable sleeve. A "bubble catcher" consisting of a section of glass tubing with a bulb was added in the plastic acid line to prevent air bubbles from injection into the titration cell. A plastic cage was erected around the system to reduce temperature fluctuations and a damping system built under the titrator to ameliorate expected vibration problems on the R/V *Vickers*.

After the titration cell had been filled and adjusted, the analytical procedures were typical of those used by other investigators. Acid doses were added using an automated burette and the resultant EMF recorded, all under computer control. All of the titration points were fit to a model of the system using a non - linear least squares approach. The alkalinity that minimized the residuals of this fit was found.

Details of the several main parts of the system and operating procedures follow.

4.2 Titration cell

Figure 2 is a schematic diagram of the titration cell. The cell bottom is a borosilicate glass Sybron/Brinkmann "90 ml" size water jacketed cell, modified by a glassblower to include a drain outlet equipped with a Teflon plug stopcock. The cell top was fabricated of plexiglass at SIO, and is attached to the bottom with an O - ring seal. The cell top has seven holes or ports with the following functions: 1) Combination glass pH electrode; 2) Glass sheathed temperature sensor (thermistor); 3) Water (sample) inlet (glass tube); 4) Glass capillary tip for acid delivery; 5) Glass vent tube for an approximately 5 ml capacity bladder made of a finger of a latex rubber surgical glove; 6) Valve made of glass rod bent to allow sealing of water inlet; 7) Glass cell vent tube with cap. All ports have O - ring seals.

The electrodes used were Radiometer combination glass pH electrodes (general use model GK2402C). This electrode, in comparison to the previously used Orion - Ross electrode, proved to be longer lasting, to have a significantly faster

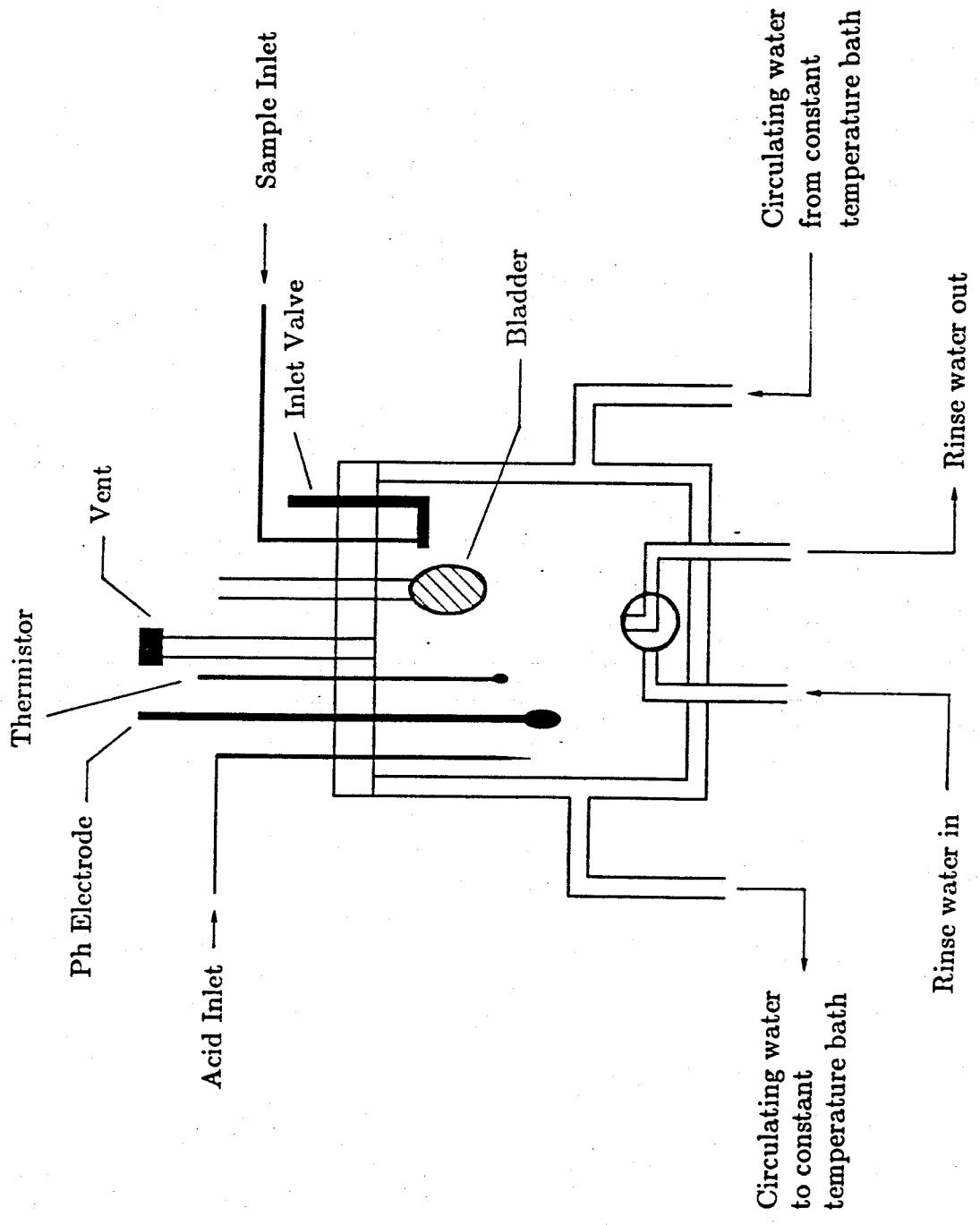


Figure 2. Schematic Diagram of Alkalinity Titration Cell

response and to be more stable. A pH meter was not used; instead, the electrode voltage output was connected to an isolation amplifier (voltage follower) that served as an impedance buffer between the electrode and a digital voltmeter.

4.3 Sample aliquoting system and calibration

Two 100 ml size glass syringes (of Japanese manufacture by "Star") were mounted on an optical bench and the syringe plungers were driven by a stepper motorized precision lead screw. Delivery of a constant volume of sample was accomplished by commanding the stepper motor to turn a preset number of counts.

Syringe volume calibrations were done by weighing deliveries of samples of known density (either pure water or sea water). The means of the pre - cruise laboratory calibrations of the syringe delivery volumes agreed with the means of the post - cruise calibrations to better than one part in 6000. Four sets of calibrations of both syringes were made at sea by delivering sea water samples of known salinity into pre - weighed bottles. The bottles were sealed with rubber septums and later weighed in the shore laboratory. Six deliveries were done for each calibration set; the sample standard deviation for each set was better than one part in 5000. All of the sets agreed with the laboratory calibrations to within one part in 1800. The sets on the left side agreed to better than one part in 3600; those on the right side, to one part in 2300 on average. The ALK data reported here were calculated using the pre - cruise volume calibrations for the syringes (91.151 ml for the left side syringe, serial number 7736; and 91.210 ml for the right side syringe, serial number 7754). The average for all shore calibrations (APR 91 to MAR 94) of the left side syringe is 91.150 ml ($\pm 1/10000$ for 7 sets); for the right side syringe, the average is 91.181 ml ($\pm 1/2800$ for 9 sets). A possible future small adjustment to the data would be to use the overall average volume for the right side, which agrees to one part in 7000 with the shipboard values. This change would raise the right side ALK's by one part in 3000. No significant change based on the calibration data would be possible for the left side results.

4.4 Acid titrant delivery system and calibration

The acid titrant was 0.1N hydrochloric acid in an aqueous sodium chloride matrix of approximately 0.7 ionic strength. Doses of acid were added to the titration cell under computer control from a Metrohm Dosimat 665 automatic burette. The plastic acid line from the Dosimat (5 ml size burette) was connected to a capillary glass tip for entrance into the titration cell.

A total of 26 doses were made during a titration, with a total of 3.4 ml of added acid titrant. Prior to and after the second (bicarbonate) equivalence point, the doses were of 200 microliters. Around the equivalence point, from 2.0 ml to 2.6 ml, the doses were of 50 microliters in order to weigh the titration curve fit to that region for total alkalinity determination.

The acid titrants were prepared in batches (designated batch numbers 9 and 11) of 20 liters and bottled in one liter reagent bottles with greased stoppers. During the cruise ten different bottles of acid were used. Bottles were changed when half empty. Three pairs of acid batch 11 bottles were used on Leg 1. After the first few days of Leg 2, two pairs of batch 9 bottles were used until the end of the cruise.

Acid densities were measured with a pycnometer at two different temperatures, 21 and 25 °C. A linear equation, using a universal slope of 0.28261, was used to calculate the acid density for a titration according to the temperature measured with a thermistor (surface probe) attached to the glass Dosimat burette.

The acid titrant concentration was determined by titration of sodium carbonate solutions. These were prepared by solution in purified water of primary standard sodium carbonate heated to constant weight at 270 °C. Titrations of standard carbonate were done on two bottles of acid batch 9, one prior to the cruise and one during the period of the cruise, and on one bottle of acid batch 11, during the cruise. These titrations were performed on the shore based gravimetric titration system in the CDRG laboratory at SIO (Guenther et al, 1994a). Results are summarized in the following table:

Date	STD Bottle-Trial	Acid Bottle No.	[HCl](eq/kg)
23 May 91	59-2	9D	0.09731
23 May 91	60-2	9D	0.09725
1 Sep 92	69-4	9B	0.09729
1 Sep 92	70-3	9B	0.09724
28 Aug 92	70-2	11C	0.09709
31 Aug 92	68-3	11C	0.09698
31 Aug 92	69-2	11C	0.09712

The average of the four determinations of acid batch 9 is 0.09727 ± 0.00033 equivalents per kilogram (eq/kg). The value used to calculate the reported data is a preliminary value of 0.09724 eq/kg, representing about 0.75 microequivalents per kilogram ($\mu\text{eq}/\text{kg}$) difference in calculated alkalinity. Pending further retrospective analysis of the acid calibrations, it was not deemed worthwhile to adjust the tabulated data. The average of the three determinations of batch 11 is 0.09706 ± 0.00007 eq/kg. The value used to calculate the reported data is a preliminary value of 0.09690 eq/kg, representing about 3.8 $\mu\text{eq}/\text{kg}$ difference in calculated alkalinity. This latter value was determined before the cruise by titrating water from a number of bicarbonate quality assessment bottles (STD batch A) with both batch 9 and batch 11 acids, and then choosing an acid concentration for batch 11 that produced the same concentration for STD A as obtained with batch 9. If the average batch 11 value from the above table is used, an offset would appear in the quality assessment standards when batch 9 acid was substituted on Leg 2; the offset would be such that the quality assessment standards would agree less well with the shore based results on the gravimetric system. If the preliminary batch 11 value is used, no offset is discernible when the acids were changed. For that reason, pending further analysis, we have not used the sodium carbonate calibrations of acid batch 11 listed in the above table.

4.5 Temperature measurement and calibration

Several temperatures were measured in the titration procedure, using YSI thermistor probes. The aliquot temperature was measured with a surface probe attached to the outside surface of the syringe. This temperature was read and recorded in the data set when a key was pressed on the computer after the water had been in the syringe for at least ten minutes and just before injection of the aliquot into the titration cell. The acid temperature was measured with a surface probe attached to the Dosimat burette and recorded for every dose of titrant. The average temperature during the titration was used for calculation of the acid density. The cell temperature was measured with a glass sheathed immersion probe and recorded for every dose. The temperature at the midpoint of the titration was used in the calculation of alkalinity. The ambient air temperature was measured with an air probe during the titration and recorded, but not used in the calculations.

Thermistors were calibrated at the Oceanographic Data Facility of SIO by comparison to standard thermometers, with the assistance of Mr. Robert Williams. One set of calibrations was done prior to the cruise, in summer 1992. Calibration curves for the probes were very close to those done prior to the TUNES Leg 3 cruise, in summer 1991.

4.6 *Data acquisition system*

The titrator had two identical computerized data acquisition systems, one for each side of the titrator. The thermistor resistances and the electrode voltage (after passing through the isolation amplifier) were measured with a 5 1/2 digit Hewlett Packard digital multimeter. The electrode voltages were measured on the ± 300 mv scale and recorded to 0.01 mv. A switching box and scanner allowed the multiple inputs to be recorded on hard disc under program control of a Zenith 286 lap top computer equipped with a data acquisition expansion chassis. The operating program also controlled the addition of acid titrant doses by the Dosimat burette.

At the end of a titration, recorded data were copied to a 3 1/2" HD diskette for archiving and later calculation of the alkalinity. One saved file contains one set of data for each titration point, i.e. the final stable electrode EMF's and associated temperatures. Another saved file contains 1/2 second averages of the electrode EMF's throughout the titration, allowing the electrode behavior and stability for every titration to be recreated.

4.7 *Calculation of titration alkalinity*

The titration alkalinity, ALK, was calculated from the titration data set using a non -linear least squares fit of the entire titration curve. A description of this procedure is given in the Department of Energy Handbook of Methods (DOE, 1994). In this procedure, the residuals of the fit are minimized by adjustment of four parameters: the bicarbonate equilibrium constant, K1; the ALK; the DIC; and f, related to the E0 of the system. Codes entered by the operator identified the sample as either sea water or bicarbonate in sodium chloride solution and the appropriate constants and densities were then selected by the program.

The sets of chemical equilibrium constants used in the fit routine to calculate the alkalinity were as follows:

For 0.7M NaCl:	K1 (bicarbonate)	: Dyrssen and Hansson	(1972)
	K2 (carbonate)	: Dyrssen and Hansson	(1972)
	Kw (water)	: Dyrssen and Hansson	(1972)
For sea water:	K1 (bicarbonate)	: Dickson and Millero	(1985)
	K2 (bicarbonate)	: Dickson and Millero	(1985)
	Kw (water)	: Dickson and Riley	(1979)
	Kb (borate)	: Johansson and Wedborg	(1981)
	Ks (sulfate)	: Khoo et. al.	(1977)
	Kf (fluoride)	: Dickson and Riley	(1979)
relation to SAL:	Total borate	: Uppstrom	(1974)
	Total sulfate	: Morris and Riley	(1966)
	Total fluoride	: Riley	(1965)

Phosphate and silica were assumed to be equal to zero. According to Dickson (DOE, 1994), this assumption has a negligible effect on the calculated alkalinity.

For every titration a graph was produced that displayed the residuals of the fit versus the actual data. Titration data files were copied into a master computer directory to allow refits of the titration data after final calibrations and adjustments to the data. All data, including the 1/2 second averages, have been archived at SIO.

4.8 Titrator operating procedure

Two bottles of water to be analyzed are placed in holders above the syringe driver assembly and allowed to adjust to ambient temperature. Residual prior samples are emptied from the syringes using the three way valves at the tips. The syringes and connective tubing are filled and emptied with small volumes of new samples, then the syringes are allowed to fill through a mostly glass (Tygon connection pieces) tubing system from the bottoms of the sample bottles.

The titration cells and water delivery tubing are prepared by a rinsing and flushing procedure. First the caps are removed from the cell vent tubes. The previous samples of acidified water are drained from the cells, then the cells are rinsed with purified water. The glass tubing leading from the syringes to the cells are flushed simultaneously with preset injections of 15 ml, using the syringe driver mechanism. The syringes are now set at a constant starting point. The valves at the sample inlets to the cells are closed. The cells are rinsed two more times and allowed to soak for a few minutes while stirring. The acid titrant tips in the cells are flushed with injections of 50 microliters; and the cells are drained then rinsed again to just below the acid tips. The cell drain stopcocks are closed and the

syringe delivery tubing again opened to the cells. The cells are now ready to be filled with samples. The computers are signaled to record the current temperatures of the surface thermistor probes attached to the outside surfaces of the syringes: these temperatures are used as the aliquot temperatures. The syringe driver motor is switched on to move the syringes a constant distance for simultaneous injection of aliquots into both cells. The sample entry tubes in the cells are closed with the valves. The submerged bladders are inflated using rubber pipette bulbs to reduce the cell air spaces to a minimum volume, one to two cc including the visible bubble and the volume of the cell vent tube. The cells are then closed by placing air tight plastic caps on the cell vent tubes. The bulbs are removed from the tubes leading to the bladders so that the insides of the bladders remain at atmospheric pressure during the titrations. The stirrers are turned on and the cells allowed to equilibrate to the operating temperature maintained by flowing water from a refrigerated constant temperature bath through the water jackets on the cells.

The computer data acquisition program prompts the operator to enter sample identification, sample type (sea water or bicarbonate in sodium chloride solution), and salinity. The "salinities" assigned to the bicarbonate reference materials were 39.39 for SIO STD batch A and 38.15 for SIO STD batch B. The salinity used for the natural sea water Certified DIC Reference Material, batch number 13, was 32.864 (A. Dickson, private communication). All of these apparent salinities were calculated from pycnometer density measurements using an equation of state for sea water (Fofonoff, 1985). When temperature stability has been reached, in about ten minutes, the titration programs are started and the first doses added. At each point on the titration curve, the program evaluates the electrode output stability according to a preset criterion. When stability is reached, the electrode EMF and the cell, acid burette and ambient air temperatures are recorded and the next dose of acid is injected.

The complete analysis cycle is about 30 minutes long; thus, about four titrations can be completed per hour, with dual titrators.

4.9 Daily analysis schedule

With two operators on board ship, the titrator was operated essentially around the clock during the cruise, interrupted by water sampling activities on station. An average of 37 titrations per analysis day were run. The usual analysis sequence was as follows. Before and after every eight sets of sea water samples (16

titrations), a set of reference materials for quality assessment were run. These reference materials were bicarbonate solutions prepared by the CDRG at SIO. These solutions were prepared in 50 liter batches by bubbling ambient air through solutions of sodium carbonate in 0.7 ionic strength sodium chloride until the pH reached stability. One liter borosilicate glass bottles were filled with solutions from two batches (designated STD batches A and B). Normally five titrations were performed on each bottle during the cruise. Each time these reference materials were titrated they were switched side to side on the system. Once a day, approximately every 40 titrations, a pair of bottles of Dr. Andrew Dickson's Certified DIC Reference Material Batch No. 13 were titrated. This batch was prepared from natural sea water. Normally one analysis was done on each CRM bottle after a DIC analysis had been made on the SOMMA coulometric system. Twice a day duplicate sea water samples collected on profile stations were titrated, one bottle of the pair on each side of the titrator. Samples were normally analyzed in order of depth, from shallow to deep. Thus on one day of 40 titrations there would be two pairs of STD's and one pair of CRM's in addition to 17 pairs of collected sea water samples, including two pairs of duplicate samples.

5. Summary of Results

5.1 Data quality assessments

5.1a Duplicate sea water samples

During each leg of the cruise thirty six pairs of duplicate samples were collected and analyzed, i.e. two sample bottles were filled with water from the same Niskin bottle. The bottle pairs were titrated together, one bottle on the right side of the titrator and the other on the left. The sample standard deviations calculated from the pair data, assuming the left and right sides were not systematically different, are summarized in the following table:

Leg	No. of duplicate pairs	$s, \mu\text{eq}/\text{kg}$
1	33	1.56
2	30	2.13

For Leg 1, one duplicate pair was flagged (identified malfunction or error) and one pair was omitted from consideration by the three sigma criterion (side to side delta of $11.7 \mu\text{eq}/\text{kg}$). For leg 2, three pairs were flagged and the data record

was lost for one pair. Two pairs were omitted by the three sigma criterion (delta's of 12.5 and 9.9 $\mu\text{eq}/\text{kg}$).

5.1b SIO bicarbonate reference materials

A total of 86 titrations on bottles of STD batch A were done on both legs. Eleven were omitted from consideration due to operator error or titrator malfunction and by the three sigma criterion (one result: 11.2 $\mu\text{eq}/\text{kg}$ low). For batch B, there were 92 total titrations, with two omissions (including one greater than three times sigma at 7.2 $\mu\text{eq}/\text{kg}$ low). The results are summarized in the following table:

STD Batch	No. of analyses	Avg. ALK	Sample std dev ($\mu\text{eq}/\text{kg}$)
A	75	2304.24	2.77
B	90	2298.75	2.03

In comparison, analyses of samples of these batches of STD were made before and after the cruise in the shore laboratory on the gravimetric titration system, with the following results:

STD Batch	No. of analyses	Avg. ALK	Sample std dev ($\mu\text{eq}/\text{kg}$)
A	26	2307.03	1.59
B	26	2302.15	1.94

We have not determined the reason why the shore data are higher than the shipboard data.

Figures 3 and 4 are versions of control charts for the shipboard STD data. The individual results are plotted for each STD batch, with the overall mean and the two times and three times standard deviation levels shown. Six of the omitted data points are plotted on the STD A chart - the six points greater than the three times level. All of the other omitted data are off the scale of the chart. One of the omitted data points is plotted on the STD B chart - the only one below the three times level.

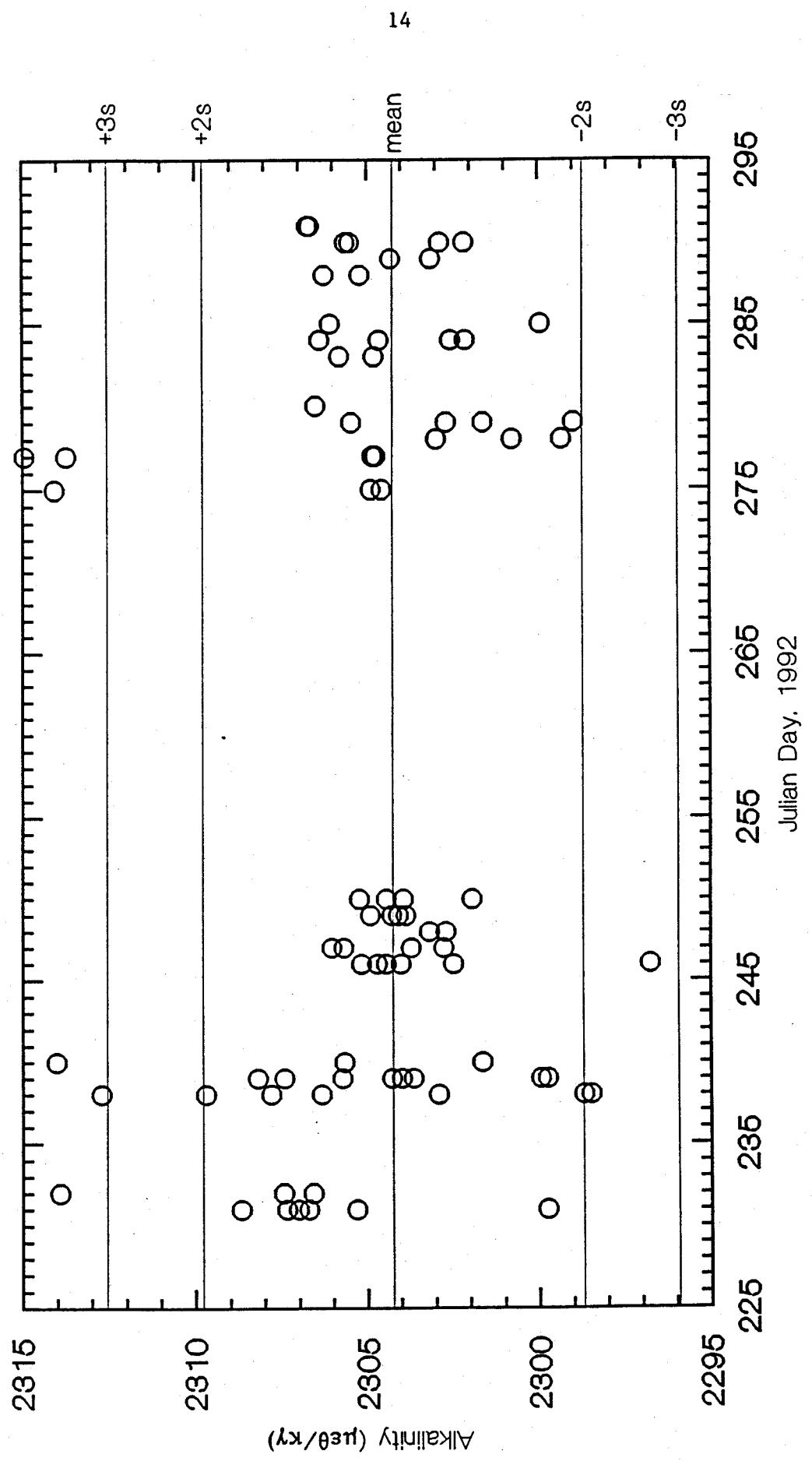


Figure 3: Control chart for CDRG Bicarbonate Reference Material Batch A shipboard alkalinity data from CGC92 Legs 1 and 2 (WOCE line P13). Average alkalinity for batch A: 2304.24 \pm 2.77 $\mu\text{eq}/\text{kg}$ for 75 analyses.

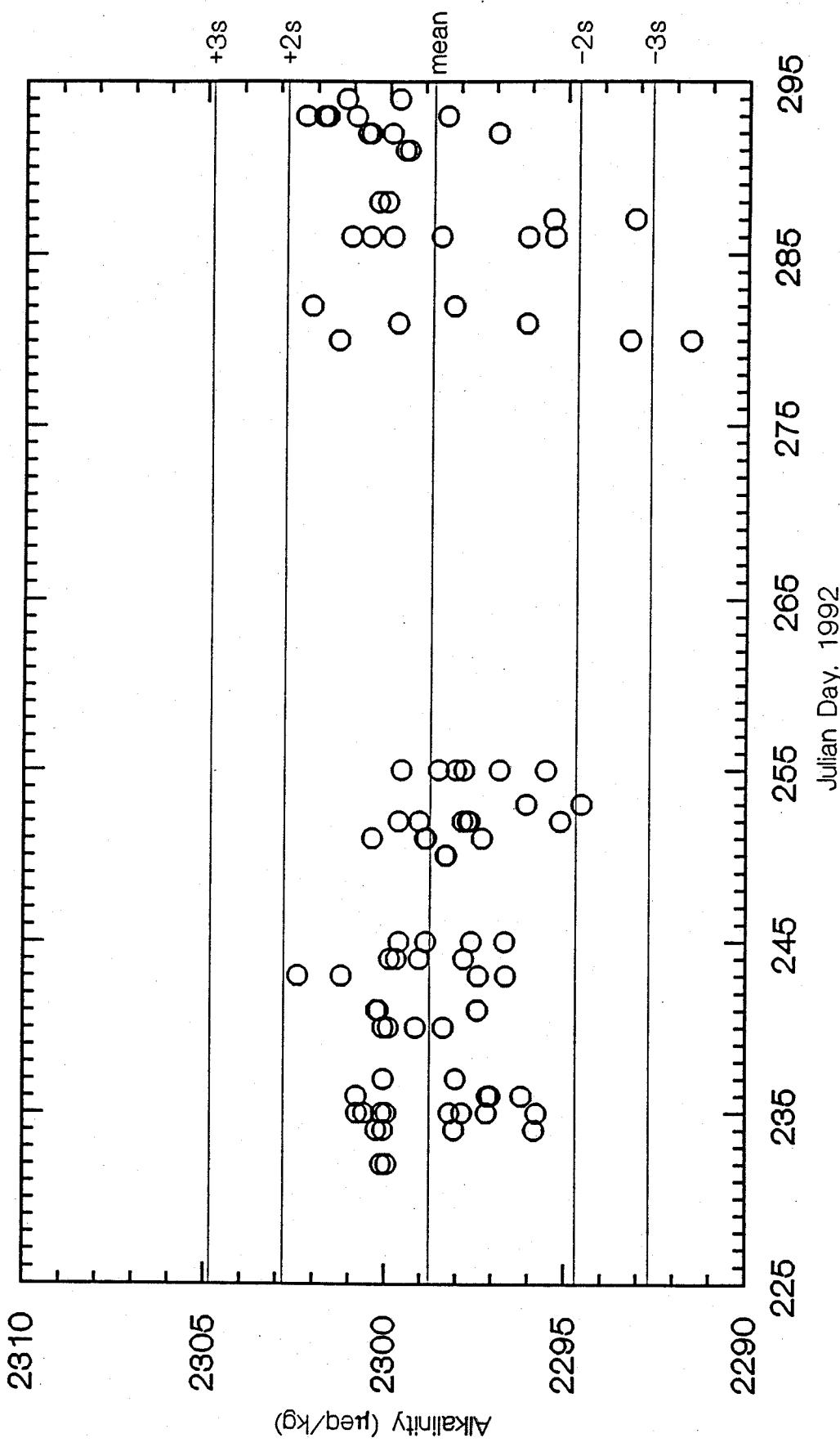


Figure 4: Control chart for CDRG Bicarbonate Reference Material Batch B shipboard alkalinity data from CGC92 Leg 1 and 2 (WOCE line P13). Average alkalinity for batch B: 2298.75 \pm 2.03 $\mu\text{eq}/\text{kg}$ for 90 analyses.

5.1c CRM sea water reference materials, batch 13

A total of 84 titrations of CRM batch 13 samples were done during the cruise. In most cases aliquots had previously been removed from the CRM bottles for coulometric DIC analysis. Six titrations were omitted from consideration due to operator error or instrument malfunction and by the three times sigma criterion (two results, at 15.0 $\mu\text{eq}/\text{kg}$ high and 19.0 $\mu\text{eq}/\text{kg}$ low). At the shore laboratory, 6 titrations were made on this batch of CRM on the gravimetric titration system. One was omitted. These results are shown in the following table:

Titrator	No. of analyses	Avg. ALK ($\mu\text{eq}/\text{kg}$)	Sample std dev ($\mu\text{eq}/\text{kg}$)
volumetric (sea)	78	2201.26	2.29
gravimetric(shore)	5	2198.67	3.87

Figure 5 is a control chart for the shipboard analyses of CRM batch 13 samples.

5.1d Discussion of data quality

Multiple titrations of duplicate sea water samples, CRM's and STD's during the cruise demonstrate that the imprecision of the shipboard titration system for the CGC92 cruise is at the level of approximately 2.5 microequivalents per kilogram (one standard deviation). The three types of quality assessment samples titrated actually give different results. The duplicate sea waters yield a standard deviation of a single measurement (s) of 1.6 $\mu\text{eq}/\text{kg}$ on Leg 1 and 2.1 on Leg 2. The two bicarbonate STD reference materials do not agree well. Batch A has the highest standard deviation at 2.8 $\mu\text{eq}/\text{kg}$ overall, but batch B is significantly lower at 2.0. Moreover, the scatter in STD A decreased on Leg 2 in comparison with Leg 1, while STD B increased, as did the other quality assessment samples. The primary reason for the general increase in scatter on this cruise, in comparison to the TUNES Leg 3 cruise the previous year, is the frequent appearance of significant bias between the two sides of the titrator. The bias varied to some extent, and fortuitously had a larger effect on the STD A set than the other quality assessment data sets. The side to side bias also became more severe on Leg 2, accounting for the general increase in scatter from Leg 1 to Leg 2. We have not been able to identify the cause of the side to side bias. On average it was about $1.8 \pm 2.3 \mu\text{eq}/\text{kg}$, right side being higher, as determined from 172 runs of the

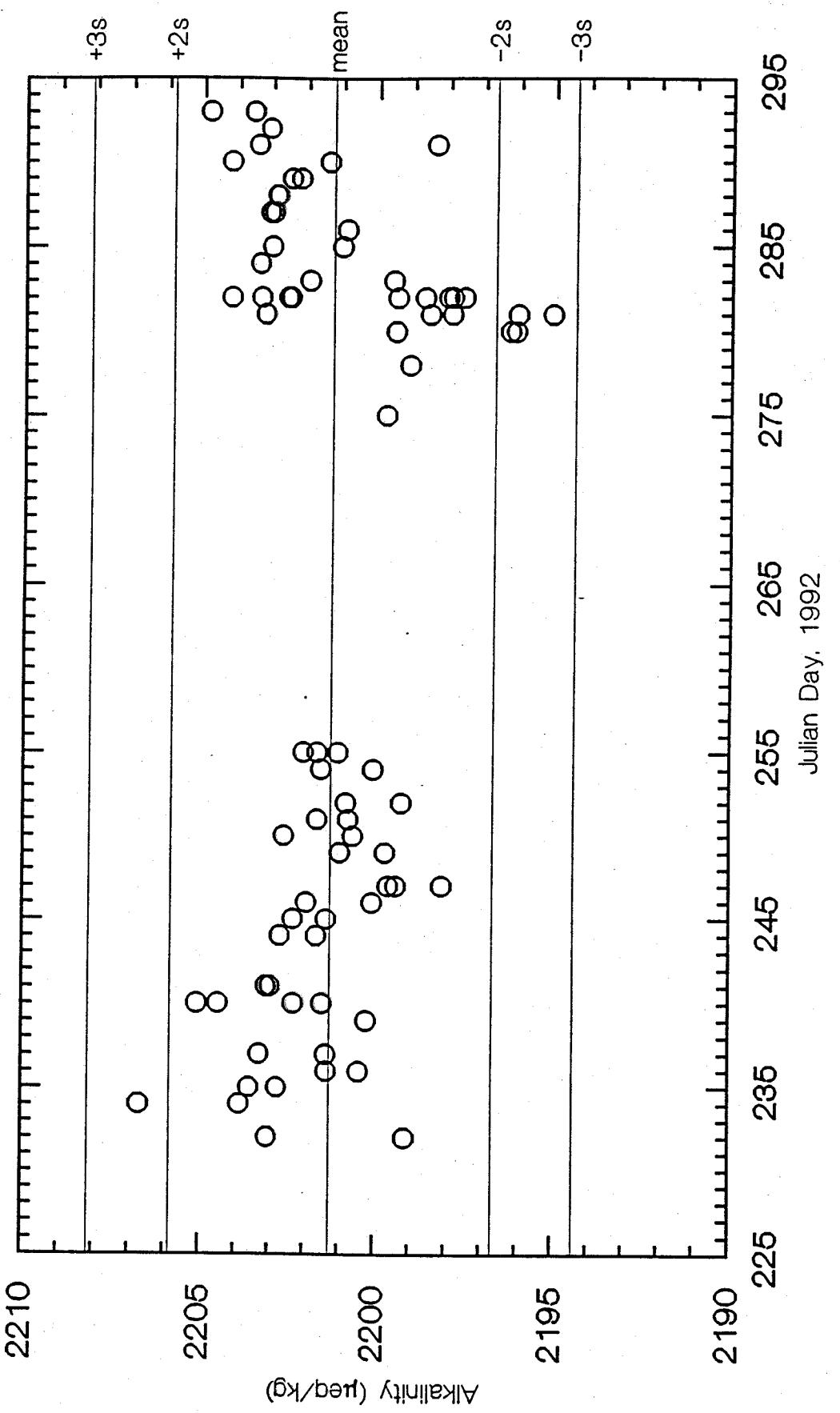


Figure 5: Control chart for SiO Certified DIC Reference Material Batch 13 shipboard alkalinity data from CGC92 Legs 1 and 2 (WOCE line P13). Average alkalinity for CRM 13: 2201.26 \pm 2.29 $\mu\text{eq}/\text{kg}$ for 78 analyses.

"same" water simultaneously on both sides of the titration system, i.e. for duplicate sea water samples run side by side, and also for CRM's and STD's run side by side.

Comparison of CRM and STD results at sea on the volumetric titrator to those in the shore laboratory obtained on the gravimetric titrator reveals an offset between the two systems. For STD A, the shore results are on average 2.8 $\mu\text{eq}/\text{kg}$ higher than the shipboard results, and for STD B, the shore results are 3.5 higher. The side to side offset tends to be averaged out for these comparisons. For CRM 13, the few shore results are on average 2.6 $\mu\text{eq}/\text{kg}$ lower than the shipboard results. The standard deviation for the shore CRM results is very high, however, with the data set split between low numbers and others higher than the shipboard result.

The lack of a definitive calibration of the acid titrant batch 11 (see section 4.4 above) implies another possible source of systematic error. As discussed above, the concentration of acid 11 was chosen to produce results for bicarbonate STD reference materials that agreed with those obtained using acid batch 9, for which the acid calibration is better and shows consistency with other results, as discussed in Guenther et al. (1994b). Some further scrutiny of the data may result in an improvement of the results in this area.

In conclusion, it can be stated that influences due to temperature, density and volume measurements on the accuracy of the results are likely to be small, close to the analytical imprecision, based on results reported here. The side to side bias in the titrator system seen in this cruise could lead to a systematic error of up to 2 $\mu\text{eq}/\text{kg}$ in a single sea water result, although the sign of this possible error is as yet unknown. The offset between bicarbonate STD reference materials analyzed at sea and in the shore laboratory indicates that the shipboard results may be up to 3 $\mu\text{eq}/\text{kg}$ low. The question of the accuracy of the acid calibration and indeed of the titration method overall is less clear due to the lack of a Certified Reference Material for ALK. Interlaboratory comparisons indicate that the accuracy level may be $\pm 10 \mu\text{eq}/\text{kg}$ or more.

5.2 *Data tabulations of shipboard alkalinity results*

5.2a Sea water sample data

The table lists results from all titrations in the data set. The seventh column, headed TRIAL, lists the sequential number of the titration on the same sample bottle of water. In most cases, only one was made. The "A" and "B" refer to

duplicate samples collected from the same Niskin bottle. The eighth column, headed FLAG, identifies with an "X" those calculated titrations that were affected by identified operator error or titrator system malfunctions. Such problems included: 1) Loss of water during filling of the titration cell (sometimes identified after the titration had been run); 2) problems with the pH electrodes or isolation amplifiers, often evidenced by poor residuals on the titration fit; 3) operator mistakes, such as forgetting to turn on the stir bar or to close the drain or inlet valves. The titrations identified with the flag "EX" refer to those titrations off by a large margin, usually 20 $\mu\text{eq}/\text{kg}$ or more, presumably due to operator error or system malfunction, but not identified. The ninth column, headed TRIAL ALK, is the individual result for one titration trial. The tenth column, headed TRIAL DELTA, is the difference between good trials on aliquots from a single sample of water. The eleventh column, headed BOTTLE ALK, is the average of all the good trials made on water from one bottle. The twelfth column, headed BOTTLE DELTA, is the difference between analyses of water from duplicate sample bottles. The thirteenth column, headed "NISKIN" AVG is the average alkalinity obtained for a single Niskin bottle. In most cases, with a single titration per Niskin bottle, columns nine, eleven and thirteen are identical, and nothing appears in columns ten and twelve.

5.2b SIO bicarbonate reference material data

Two tables report the shipboard alkalinity results for the SIO bicarbonate reference materials, designated STD A and STD B. The tables are arranged in order of analysis date during the cruise. The individual bottles of each batch are identified by a number after the A or B. The third column, headed TRIAL, is the sequential number of the titration on the same bottle of water. The fourth column, headed FLAG, identifies with an "X" those calculated titrations that are affected by identified operator error or titrator system malfunctions (same examples as listed above). Bottle number A2, titrated on 1 and 3 Oct 92 was given an "X" flag on all five titrations because the bottle was a "bad" one, consistently high by 10 $\mu\text{eq}/\text{kg}$. The titrations identified with the flag "EX" refer to those titrations off by a large margin, 30 $\mu\text{eq}/\text{kg}$ or more, presumably due to operator error or system malfunction, but not identified. The fifth, sixth and seventh columns list the individual trial alkalinites and the overall average and sample standard deviation of all the alkalinity titrations of the STD batch during the cruise.

5.2c CRM sea water reference material data

The last table reports the shipboard alkalinity results for Certified DIC Reference Materials, batch number 13. The columns have the same meaning as described above for the SIO reference materials. The letters following the CRM sample bottle number are used for internal accounting purposes.

References

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THE CARBON DIOXIDE PROJECT OF THE SCRIPPS INSTITUTION OF OCEANOGRAPHY
CGC92 Legs 1 and 2 CDRG SHIPBOARD ALKALINITY REPORT

14-OCT-94

SUMMARY OF ALKALINITY DATA

STN	CAST NISK	DEPTH (dbar)	SAMPLE DATE	ANALYSIS DATE	SAMPLE BOTTLE	TRIAL	FLAG	TRIAL ALK	TRIAL DELTA	BOTTLE "NISKIN"	BOTTLE ALK	BOTTLE DELTA	BOTTLE AVG	(EQUIV/KG SW)	
5	1 36	9	17AUG92	18AUG92	2631 A	1		2240.76	+0.25	2240.89	2241.01	-0.57	2244.43	2244.43	
5	1 36	9	17AUG92	18AUG92	2631 B	1		2241.01		2241.25	2241.25		2241.25	2241.25	
5	1 34	24	17AUG92	18AUG92	2630	1		2241.25		2248.64	2248.64		2248.64	2248.64	
5	1 33	60	17AUG92	18AUG92	2629	1		2248.64		2251.85	2251.85		2251.85	2251.85	
5	1 32	75	17AUG92	18AUG92	2628	1		2251.85		2253.58	2253.58		2253.58	2253.58	
5	1 31	99	17AUG92	18AUG92	2627	1		2253.58		2256.40	2256.40		2256.40	2256.40	
5	1 30	148	17AUG92	18AUG92	2626	1		2256.40		2260.96	2260.96		2260.96	2260.96	
5	1 29	199	17AUG92	18AUG92	2625	1		2260.96		2274.72	2274.72		2274.72	2274.72	
5	1 28	248	17AUG92	18AUG92	2624	1		2274.72		2293.02	2293.02		2293.02	2293.02	
5	1 27	301	17AUG92	18AUG92	2623	1		2293.02		2302.19	2302.19		2302.19	2302.19	
5	1 26	348	17AUG92	18AUG92	2622	1		2302.19		2311.88	2311.88		2311.88	2311.88	
5	1 25	397	17AUG92	18AUG92	2621	1		2311.88		2328.16	2328.16		2328.16	2328.16	
5	1 24	488	17AUG92	19AUG92	2620	1		2328.16		2340.62	2340.62		2340.62	2340.62	
5	1 23	597	17AUG92	19AUG92	2619	1		2340.62		2352.83	2352.83		2352.83	2352.83	
5	1 22	697	17AUG92	19AUG92	2618	1		2352.83		2362.14	2362.14		2362.14	2362.14	
5	1 21	798	17AUG92	19MAY92	2617	1		2362.14		2369.52	2369.52		2369.52	2369.52	
5	1 20	897	17AUG92	19AUG92	2616	1		2369.52		2378.28	2378.28		2378.28	2378.28	
5	1 19	999	17AUG92	19AUG92	2615	1		2378.28		2383.53	2383.53		2383.53	2383.53	
5	1 18	1099	17AUG92	19AUG92	2614	1		2383.53		2388.56	2388.56		2388.56	2388.56	
5	1 17	1185	17AUG92	19AUG92	2613	1		2388.56		2393.71	-1.81		2394.61	2394.61	
5	1 16	1296	17AUG92	19AUG92	2612	1		2393.71		2405.92	2405.92		2405.92	2405.92	
5	1 16	1298	17AUG92	19AUG92	2612	2		2405.92		2410.18	2410.18		2410.18	2410.18	
5	1 14	1498	17AUG92	19AUG92	2611	1		2410.18		2413.01	2413.01		2413.01	2413.01	
5	1 13	1598	17AUG92	19AUG92	2610	1		2413.01		2414.97	2414.97		2414.97	2414.97	
5	1 12	1697	17AUG92	19AUG92	2609	1		2414.97		2419.55	2419.55		2419.55	2419.55	
5	1 11	1799	17AUG92	19AUG92	2608	1		2419.55		2424.31	2424.31		2424.31	2424.31	
5	1 10	1997	17AUG92	19AUG92	2607	1		2424.31		2427.75	2427.75		2427.75	2427.75	
5	1 09	2196	17AUG92	19AUG92	2606	1		2427.75		2431.96	2431.96		2431.96	2431.96	
5	1 08	2399	17AUG92	19AUG92	2605	1		2431.96		2436.43	2436.43		2436.43	2436.43	
5	1 08	2798	17AUG92	19AUG92	2604	1		2436.43		2435.86	2435.86		2435.86	2435.86	
5	1 06	3000	17AUG92	19AUG92	2603	A		2436.43		2440.22	2440.22		2440.22	2440.22	
5	1 05	3000	17AUG92	19AUG92	2603	B		2436.43		2438.66	2438.66		2438.66	2438.66	
5	1 03	3102	17AUG92	19AUG92	2602	1		2438.66		2224.14	2224.14		2224.14	2224.14	
5	1 01	3310	17AUG92	19AUG92	2601	1		2224.14		2225.12	2225.12		2225.12	2225.12	
6	6	1 09	10	21AUG92	21AUG92	2632	1		2225.12		2226.51	2226.51		2226.51	2226.51
6	7	1 15	10	21AUG92	21AUG92	2633	1		2226.51		2244.43	2244.43		2244.43	2244.43
8	8	1 25	9	21AUG92	21AUG92	2658	1		2244.43		2255.09	2255.09		2255.09	2255.09
8	8	1 24	24	21AUG92	21AUG92	2657	A		2255.09		2246.81	2246.81		2246.81	2246.81
8	8	1 24	24	21AUG92	21AUG92	2657	B		2246.81		2257.00	2257.00		2257.00	2257.00
8	8	1 23	50	21AUG92	21AUG92	2656	1		2257.00		2244.47	2244.47		2244.47	2244.47
8	8	1 22	74	21AUG92	21AUG92	2655	1		2244.47		2250.60	2250.60		2250.60	2250.60
8	8	1 21	106	21AUG92	21AUG92	2654	1		2250.60		2249.83	2249.83		2249.83	2249.83
8	8	1 20	124	21AUG92	21AUG92	2653	1		2249.83		2268.13	2268.13		2268.13	2268.13
8	8	1 19	148	21AUG92	21AUG92	2652	1		2268.13		2288.00	2288.00		2288.00	2288.00
8	8	1 18	198	21AUG92	21AUG92	2651	1		2288.00		2298.97	2298.97		2298.97	2298.97
8	8	1 17	248	21AUG92	21AUG92	2650	1		2298.97		2305.07	2305.07		2305.07	2305.07
8	8	1 16	299	21AUG92	21AUG92	2649	1		2305.07		2316.47	2316.47		2316.47	2316.47
8	8	1 15	348	21AUG92	21AUG92	2648	1		2316.47		2324.00	2324.00		2324.00	2324.00

13	74	23AUG92	2244.53	2244.53
1 33	1 32	23AUG92	2250.14	2250.14
1 33	1 31	23AUG92	2260.82	2260.82
1 33	1 30	23AUG92	2282.76	2282.76
1 33	1 29	23AUG92	2298.15	2298.15
1 33	1 28	23AUG92	2302.27	2302.27
1 33	1 27	23AUG92	2308.82	2308.82
1 33	1 26	23AUG92	2321.51	2321.51
1 33	1 25	23AUG92	2331.33	2331.33
1 33	1 24	23AUG92	2336.03	2336.03
1 33	1 23	23AUG92	2344.63	2344.63
1 33	1 22	23AUG92	2356.73	2356.73
1 33	1 21	23AUG92	2365.34	2365.34
1 33	1 20	23AUG92	2374.09	2374.09
1 33	1 19	23AUG92	2384.57	2384.57
1 33	1 18	23AUG92	2395.17	2395.17
1 33	1 17	23AUG92	2406.79	2406.79
1 33	1 16	23AUG92	2409.86	2409.86
1 33	1 15	23AUG92	2414.84	2414.84
1 33	1 14	23AUG92	2414.86	2414.86
1 33	1 13	23AUG92	2419.29	2419.29
1 33	1 12	23AUG92	2413.35	2413.35
1 33	1 11	23AUG92	2418.00	2418.00
1 33	1 10	23AUG92	2423.95	2423.95
1 33	1 09	23AUG92	2419.08	2419.08
1 33	1 08	23AUG92	2419.37	2419.37
1 33	1 07	23AUG92	2418.97	2418.97
1 33	1 06	23AUG92	2418.41	2418.41
1 33	1 05	23AUG92	2415.12	2415.12
1 33	1 04	23AUG92	2411.12	2411.12
1 33	1 03	23AUG92	2415.41	2415.41
1 33	1 02	23AUG92	2415.32	2415.32
1 33	1 01	23AUG92	+4.29	2413.27
1 33	1 00	23AUG92	2415.32	2415.32
1 33	1 03	24AUG92	+1.44	2239.53
1 33	1 02	24AUG92	-6.54	2223.71
1 33	1 01	24AUG92	2224.38	2224.38
1 33	1 00	24AUG92	2227.76	2227.76
1 33	1 03	24AUG92	2226.25	2226.25
1 33	1 02	24AUG92	2228.03	2228.03
1 33	1 01	24AUG92	2229.09	2229.09
1 33	1 00	24AUG92	2235.07	2235.07
1 33	1 03	24AUG92	2240.98	2240.98
1 33	1 02	24AUG92	2240.76	2240.76
1 33	1 01	24AUG92	2251.66	2251.66
1 33	1 00	24AUG92	2251.06	2251.06
1 33	1 03	25AUG92	X	EX
1 33	1 02	25AUG92	2239.53	2239.53
1 33	1 01	25AUG92	2223.71	2223.71
1 33	1 00	25AUG92	2224.38	2224.38
1 33	1 03	25AUG92	2227.76	2227.76
1 33	1 02	25AUG92	2226.25	2226.25
1 33	1 01	25AUG92	2228.03	2228.03
1 33	1 00	25AUG92	2229.09	2229.09
1 33	1 03	25AUG92	2235.07	2235.07
1 33	1 02	25AUG92	2240.98	2240.98
1 33	1 01	25AUG92	2240.76	2240.76
1 33	1 00	25AUG92	2251.66	2251.66
1 33	1 03	25AUG92	2251.06	2251.06
1 33	1 02	25AUG92	2270.84	2270.84
1 33	1 01	25AUG92	2284.49	2284.49
1 33	1 00	25AUG92	2304.02	2304.02
1 33	1 03	25AUG92	2317.38	2317.38
1 33	1 02	25AUG92	2323.40	2323.40
1 33	1 01	25AUG92	2342.82	2342.82
1 33	1 00	25AUG92	2348.99	2348.99
1 33	1 03	25AUG92	2362.53	2362.53
1 33	1 02	25AUG92	2366.74	2366.74
1 33	1 01	25AUG92	2376.98	2376.98
1 33	1 00	25AUG92	2379.25	2379.25
1 33	1 03	25AUG92	2389.36	2389.36

1	13	1399	26AUG92	2743		2398.56	2398.56		
17	13	1598	26AUG92	2742	2407.01	2407.01	2407.01	2407.01	
17	12	1798	26AUG92	2741	2405.42	2405.42	2405.42	2405.42	
17	11	2098	26AUG92	2740	2416.86	2416.86	2416.86	2416.86	
17	16	2400	26AUG92	2739	2413.60	2413.60	2413.60	2413.60	
17	17	109	2700	26AUG92	2738	2421.82	2421.82	2421.82	2421.82
17	17	2999	25AUG92	28AUG92	2737	2416.46	2416.46	2416.46	2416.46
17	17	3302	25AUG92	28AUG92	2736	2421.37	2421.37	2421.37	2421.37
17	17	3601	25AUG92	28AUG92	2735	2417.23	2417.23	2417.23	2417.23
17	17	3902	25AUG92	28AUG92	2734	2420.54	2420.54	2420.54	2420.54
17	17	103	4203	25AUG92	28AUG92	2733 A	2416.84	2416.84	2420.54
17	17	101	4784	25AUG92	28AUG92	2733 B	2418.94	+2.30	2417.79
18	18	136	10	25AUG92	28AUG92	2732	2420.45	2420.45	2420.45
19	19	136	10	25AUG92	28AUG92	2731	2211.70	2211.70	2211.70
20	17	136	10	26AUG92	28AUG92	2730	2228.97	2228.97	2228.97
20	17	134	24	26AUG92	28AUG92	2800 A	2220.84	2220.84	2220.84
20	17	133	50	26AUG92	28AUG92	2800 B	2227.29	2227.29	2227.29
20	17	132	75	26AUG92	28AUG92	2799	2228.68	+1.39	2227.99
20	17	131	100	26AUG92	28AUG92	2797	2245.66	2245.66	2245.66
20	17	130	125	26AUG92	28AUG92	2796	2261.09	2261.09	2261.09
20	17	129	150	26AUG92	28AUG92	2795	2269.56	2269.56	2269.56
20	17	128	174	26AUG92	28AUG92	2794	2308.34	2308.34	2308.34
20	17	127	199	26AUG92	28AUG92	2793	2291.85	2291.85	2291.85
20	17	126	249	26AUG92	28AUG92	2792	2302.59	2302.59	2302.59
20	17	125	299	26AUG92	28AUG92	2791	2311.17	2311.17	2311.17
20	17	124	349	26AUG92	28AUG92	2790	2322.96	2322.96	2322.96
20	17	123	398	26AUG92	28AUG92	2789	2328.53	2328.53	2328.53
20	17	122	497	26AUG92	28AUG92	2788	2346.68	2346.68	2346.68
20	17	121	598	26AUG92	28AUG92	2787	2358.49	2358.49	2358.49
20	17	120	698	26AUG92	28AUG92	2786	2363.34	2363.34	2363.34
20	17	119	799	26AUG92	28AUG92	2785	2405.78	2405.78	2405.78
20	17	118	898	26AUG92	28AUG92	2784	2378.41	2378.41	2378.41
20	17	117	997	26AUG92	28AUG92	2783	2388.71	2388.71	2388.71
20	17	116	1198	26AUG92	28AUG92	2782	2395.36	2395.36	2395.36
20	17	115	1398	26AUG92	28AUG92	2781	2413.61	2413.61	2413.61
20	17	114	1699	26AUG92	28AUG92	2780	2410.93	2410.93	2410.93
20	17	113	1994	26AUG92	28AUG92	2779	2417.37	2417.37	2417.37
20	17	112	2297	26AUG92	28AUG92	2778	2413.49	2413.49	2413.49
20	17	111	2599	26AUG92	28AUG92	2777	2421.37	2421.37	2421.37
20	17	110	2899	26AUG92	28AUG92	2776	2418.84	2418.84	2418.84
20	17	109	3101	26AUG92	28AUG92	2775	2421.54	2421.54	2421.54
20	17	108	3401	26AUG92	28AUG92	2774	2417.16	2417.16	2417.16
20	17	107	3700	26AUG92	28AUG92	2773	2420.26	2420.26	2420.26
20	17	106	4002	26AUG92	28AUG92	2772	2418.76	2418.76	2418.76
20	17	105	4303	26AUG92	28AUG92	2771	2420.42	2420.42	2420.42
20	17	104	4602	26AUG92	28AUG92	2770	2416.09	2416.09	2416.09
20	17	103	4894	26AUG92	28AUG92	2769 A	2414.86	2414.86	2414.86
20	17	102	4894	26AUG92	28AUG92	2769 B	2420.41	2420.41	+6.55 2417.84
20	17	101	5821	26AUG92	28AUG92	2768	2417.35	-3.12	2418.91
20	17	100	5821	26AUG92	28AUG92	2802	2228.87	2228.87	2228.87
21	17	35	10	26AUG92	28AUG92	2803	2231.19	2231.19	2231.19
21	21	36	10	26AUG92	28AUG92	2804	2233.27	2233.27	2233.27
21	21	35	9	26AUG92	28AUG92	2805 A	2233.36	2233.36	2233.36
21	21	36	10	27AUG92	27AUG92	2837 A	2245.07	2245.07	+11.72 2239.21
21	24	36	10	27AUG92	27AUG92	2837 B	2233.58	2233.58	2233.58
21	24	34	24	27AUG92	27AUG92	2836	2236.01	2236.01	2242.89
21	24	33	48	27AUG92	27AUG92				2234.80

32	399	31AUG92	A926	2315.85
1 22	497	31AUG92	A925	2328.12
1 21	594	31AUG92	A924	2328.12
1 20	698	31AUG92	A923	2346.84
32	1 19	698	31AUG92	2346.84
32	1 18	799	31AUG92	2356.51
32	1 17	897	31AUG92	2367.58
32	1 16	997	31AUG92	2372.64
32	1 15	1197	31AUG92	2381.20
32	1 14	1397	31AUG92	2381.20
32	1 09	2906	31AUG92	2392.58
32	1 08	3100	31AUG92	2402.33
32	1 07	3402	31AUG92	2407.77
32	1 06	3701	31AUG92	2415.40
32	1 05	3999	31AUG92	2417.07
32	1 04	4402	31AUG92	2417.07
32	1 03	4802	31AUG92	2420.72
32	1 02	5201	31AUG92	2420.78
32	1 01	5663	31AUG92	2421.33
32	1 00	6063	31AUG92	2421.33
32	1 36	10	31AUG92	2421.34
34	1 36	50	01SEP92	2421.34
35	1 36	9	01SEP92	2417.52
36	1 36	10	01SEP92	2419.14
36	1 35	23	01SEP92	2421.09
36	1 35	23	01SEP92	2421.09
36	1 34	50	01SEP92	2421.09
36	1 33	75	01SEP92	2421.09
36	1 32	99	01SEP92	2421.09
36	1 31	125	01SEP92	2421.09
36	1 30	149	01SEP92	2421.09
36	1 29	174	01SEP92	2421.09
36	1 27	201	01SEP92	2421.09
36	1 26	249	01SEP92	2421.09
36	1 25	297	01SEP92	2421.09
36	1 24	356	01SEP92	2421.09
36	1 23	398	01SEP92	2421.09
36	1 22	497	01SEP92	2421.09
36	1 21	598	01SEP92	2421.09
36	1 20	697	01SEP92	2421.09
36	1 19	797	01SEP92	2421.09
36	1 18	897	01SEP92	2421.09
36	1 17	997	01SEP92	2421.09
36	1 16	1097	01SEP92	2421.09
36	1 15	1198	01SEP92	2421.09
36	1 14	1298	01SEP92	2421.09
36	1 13	1496	01SEP92	2421.09
36	1 12	1696	01SEP92	2421.09
36	1 11	1898	01SEP92	2421.09
36	1 10	2198	01SEP92	2421.09
36	1 09	2506	01SEP92	2421.09
36	1 08	2798	01SEP92	2421.09
36	1 07	3100	01SEP92	2421.09
36	1 06	3399	01SEP92	2421.09
36	1 05	3701	01SEP92	2421.09
36	1 04	4001	01SEP92	2421.09
36	1 03	4302	01SEP92	2416.60
				2416.60

41	1 15 1199	2381.13	2392.18
41	1 14 1399	2392.18	2401.49
41	1 13 1699	2401.49	2401.49
41	1 12 1899	2408.81	2408.81
41	1 11 2201	2415.48	2415.48
41	1 10 2499	2417.77	2417.77
41	1 09 2799	2419.28	2419.28
41	1 08 3101	2418.57	2418.57
41	1 07 3399	2419.93	2419.93
41	1 06 3698	2416.28	2416.28
41	1 05 4101	2418.71	2418.71
41	1 04 4504	2418.42	2418.42
41	1 03 4802	2416.86	2416.86
41	1 02 5100	2421.26	2421.26
41	1 02 5100	2420.64	2420.64
41	1 01 5492	2417.04	-0.62
41	1 01 5492	2414.95	2416.00
42	1 36 10	2263.66	2263.51
42	1 36 10	2263.35	2263.51
45	1 12 .9	2254.70	2254.70
45	1 11 .24	2256.06	2256.06
45	1 10 .51	2276.39	2276.39
45	1 09 100	2273.03	2273.03
45	1 08 198	2271.77	2271.77
45	1 07 398	2274.08	2274.08
45	1 06 799	2336.27	2336.27
45	1 05 1397	2392.30	2392.30
45	1 04 2000	2412.08	2412.08
45	1 03 2995	2418.84	2418.84
45	1 02 4001	2419.19	2419.19
45	1 01 4551	2417.54	2417.54
46	1 12 .9	2251.96	2251.96
47	1 36 11	2259.03	+0.83
47	1 36 23	2259.86	2259.45
47	1 33 48	2253.35	2253.35
47	1 32 74	2275.42	2275.42
47	1 31 98	2275.55	2275.55
47	1 30 121	2273.95	2273.95
47	1 29 148	2272.33	2272.33
47	1 27 172	2271.37	2271.37
47	1 26 198	2270.48	2270.48
47	1 25 249	2271.42	2271.42
47	1 24 299	2271.37	2271.37
47	1 23 344	2273.03	2273.03
47	1 22 398	2273.05	2273.05
47	1 21 497	2276.66	2276.66
47	1 20 599	2291.07	2291.07
47	1 19 699	2304.66	2304.66
47	1 18 797	2323.88	2323.88
47	1 17 898	2342.53	2342.53
47	1 16 997	2354.99	2354.99
47	1 15 1196	2366.74	2366.74
47	1 14 1398	2384.72	2384.72
47	1 13 1698	2395.82	2395.82
47	1 12 1998	2408.93	2408.93
47	1 11 2298	2415.32	2415.32
47	1 10 2596	2418.64	2418.64
47	1 09 2899	2420.98	2420.98
47	1 08 3200	2418.72	2418.72

1	07	3501	05SEP92	21064	2416.90	2416.90
1	06	3798	05SEP92	21063	2420.25	2420.25
1	05	4100	05SEP92	21062	2421.50	2421.50
1	04	4403	05SEP92	21061	2421.79	2421.79
1	03	4701	05SEP92	21060	2416.81	2416.81
1	02	5003	05SEP92	21059	2418.66	2418.66
1	01	5595	05SEP92	21058A	2408.07	2408.07
1	01	5595	05SEP92	21058B	2410.49	2410.49
1	01	5595	05SEP92	21058C	+2.42	2409.28
1	01	5595	05SEP92	21058D	2254.34	2254.34
1	36	9	06SEP92	21126	2253.58	2253.58
1	35	24	06SEP92	21125	2258.22	2258.22
1	34	47	06SEP92	21124A	2269.25	2269.25
1	33	70	06SEP92	21124B	2269.19	-0.06
1	32	101	06SEP92	21123	2276.85	2276.85
1	31	120	06SEP92	21122	2275.88	2275.88
1	30	148	06SEP92	21121	2271.81	2271.81
1	29	171	06SEP92	21120	2274.48	2274.48
1	28	200	06SEP92	21119	2274.36	2274.36
1	27	243	06SEP92	21118	2274.55	2274.55
1	26	300	06SEP92	21117	2276.67	2276.67
1	25	348	06SEP92	21116	2280.15	2280.15
1	24	399	06SEP92	21115	2280.64	2280.64
1	23	498	06SEP92	21114	2295.53	2295.53
1	22	599	06SEP92	21113	2311.81	2311.81
1	21	700	06SEP92	21112	2331.07	2331.07
1	20	798	06SEP92	21111	2345.64	2345.64
1	19	898	06SEP92	21110	2358.78	2358.78
1	18	996	06SEP92	21109	2371.14	2371.14
1	17	1199	06SEP92	21108	2387.76	2387.76
1	16	1399	06SEP92	21107	2398.17	2398.17
1	15	1696	06SEP92	21106	2410.83	2410.83
1	14	2009	06SEP92	21105	2413.05	2413.05
1	13	2275	06SEP92	21104	2421.24	2421.24
1	12	2802	06SEP92	21103	2418.07	2418.07
1	11	2899	06SEP92	21102	2420.15	2420.15
1	10	3198	06SEP92	21101	2417.60	2417.60
1	09	3498	06SEP92	21100	2426.75	2426.75
1	08	3796	06SEP92	21099	2419.53	2419.53
1	07	4101	06SEP92	21098	2420.02	2420.02
1	06	5003	06SEP92	21097	2412.85	2412.85
1	03	6301	06SEP92	21096	2412.27	2412.27
1	02	5501	06SEP92	21094	2406.88	2406.88
1	01	5651	06SEP92	21093A	2409.10	2409.10
1	49	6551	06SEP92	21093B	2407.10	+1.06
1	35	10	07SEP92	21127	2251.64	2251.64
1	36	9	07SEP92	21146A	2256.90	2256.90
1	34	24	07SEP92	21146B	2253.71	2253.71
1	33	48	07SEP92	21144	2272.69	2272.69
1	32	73	07SEP92	21143	2282.99	2282.99
1	31	99	07SEP92	21142	2284.58	2284.58
1	30	124	07SEP92	21141	2283.35	2283.35
1	29	150	07SEP92	21140	2283.90	2283.90
1	28	175	07SEP92	21139	2282.24	2282.24
1	27	199	07SEP92	21138	2283.66	2283.66
1	26	250	07SEP92	21137	2279.72	2279.72
1	25	298	07SEP92	21136	2282.25	2282.25
1	24	347	07SEP92	21135	2272.86	2272.86
1	23	399	07SEP92		2274.85	2274.85

51	1	22	498	07SEP92	11133	2275.08
51	1	21	598	07SEP92	21132	2290.14
51	1	20	699	07SEP92	11131	2306.14
51	1	19	798	07SEP92	21130	2306.36
51	1	18	885	07SEP92	08SEP92	2326.84
51	1	18	885	07SEP92	08SEP92	2326.84
51	1	17	998	07SEP92	08SEP92	2344.07
51	1	17	998	07SEP92	08SEP92	2345.60
51	1	16	10	08SEP92	08SEP92	2345.60
52	1	19	999	08SEP92	08SEP92	2345.60
52	1	18	1199	08SEP92	08SEP92	2345.60
52	1	17	1398	08SEP92	08SEP92	2345.60
52	1	16	1598	08SEP92	08SEP92	2345.60
52	1	16	2105	08SEP92	08SEP92	2345.60
52	1	14	2609	08SEP92	08SEP92	2345.60
52	1	13	3100	08SEP92	08SEP92	2345.60
52	1	12	3600	08SEP92	08SEP92	2345.60
52	1	11	4103	08SEP92	08SEP92	2345.60
52	1	10	4601	08SEP92	08SEP92	2345.60
52	1	09	5002	08SEP92	08SEP92	2345.60
52	1	08	5400	08SEP92	08SEP92	2345.60
52	1	07	5800	08SEP92	08SEP92	2345.60
52	1	06	6104	08SEP92	08SEP92	2345.60
53	1	25	10	08SEP92	08SEP92	2345.60
53	1	23	24	08SEP92	08SEP92	2345.60
53	1	22	48	08SEP92	08SEP92	2345.60
53	1	21	75	08SEP92	08SEP92	2345.60
53	1	20	99	08SEP92	08SEP92	2345.60
53	1	19	123	08SEP92	08SEP92	2345.60
53	1	18	150	08SEP92	08SEP92	2345.60
53	1	17	174	08SEP92	08SEP92	2345.60
53	1	16	199	08SEP92	08SEP92	2345.60
53	1	15	249	08SEP92	08SEP92	2345.60
53	1	14	300	08SEP92	08SEP92	2345.60
53	1	13	346	08SEP92	08SEP92	2345.60
53	1	12	398	08SEP92	08SEP92	2345.60
53	1	11	498	08SEP92	08SEP92	2345.60
53	1	10	600	08SEP92	08SEP92	2345.60
53	1	09	697	08SEP92	08SEP92	2345.60
53	1	08	798	08SEP92	08SEP92	2345.60
53	1	07	895	08SEP92	08SEP92	2345.60
53	1	06	997	08SEP92	08SEP92	2345.60
53	1	05	1199	08SEP92	08SEP92	2345.60
53	1	04	1398	08SEP92	08SEP92	2345.60
53	1	03	1695	08SEP92	08SEP92	2345.60
53	1	02	1998	08SEP92	08SEP92	2345.60
54	1	35	10	09SEP92	09SEP92	2345.60
54	1	13	2597	09SEP92	09SEP92	2345.60
54	1	12	2899	09SEP92	09SEP92	2345.60
54	1	11	3201	09SEP92	09SEP92	2345.60
54	1	10	3501	09SEP92	09SEP92	2345.60
54	1	09	3800	09SEP92	09SEP92	2345.60
54	1	08	4102	09SEP92	09SEP92	2345.60
54	1	07	4502	09SEP92	09SEP92	2345.60
54	1	06	4902	09SEP92	09SEP92	2345.60
54	1	05	5302	09SEP92	09SEP92	2345.60
54	1	04	5702	09SEP92	09SEP92	2345.60
54	1	03	5804	09SEP92	10SEP92	2345.60
54	1	03	5804	09SEP92	10SEP92	2345.60
					+1.53	2344.84
					+0.58	2404.15
						2403.30

57	14	1799	30SEP92	A1246	2407.70
57	1	13	2698	30SEP92	2414.15
57	1	12	2394	30SEP92	2417.91
57	1	10	2898	30SEP92	2420.65
57	1	09	2993	30SEP92	2421.61
57	1	08	3301	30SEP92	2420.99
57	1	08	3600	30SEP92	2418.91
57	1	07	3902	30SEP92	2417.56
57	1	06	4203	30SEP92	2415.07
57	1	05	4500	30SEP92	2411.91
57	1	04	4803	30SEP92	2408.31
57	1	03	5101	30SEP92	2403.82
57	1	02	5404	30SEP92	2399.44
57	1	01	5689	30SEP92	2401.89
57	1	01	5689	30SEP92	2403.99
59	1	34	49	010CT92	2307.73
59	1	33	75	010CT92	2304.95
59	1	33	75	010CT92	2366.39
59	1	32	106	010CT92	2311.92
59	1	31	123	010CT92	2309.29
59	1	30	149	010CT92	2302.40
59	1	29	169	010CT92	2297.36
59	1	28	198	010CT92	2286.30
59	1	27	260	010CT92	2276.98
59	1	26	300	010CT92	2270.51
59	1	25	347	010CT92	2282.41
59	1	24	397	010CT92	2266.91
59	1	23	498	010CT92	2276.17
59	1	22	598	010CT92	2298.02
59	1	21	697	010CT92	2325.02
59	1	20	798	010CT92	2341.60
59	1	19	895	010CT92	2357.35
59	1	18	998	010CT92	2366.52
59	1	17	1099	010CT92	2394.64
59	1	16	1298	010CT92	2391.18
59	1	15	1498	010CT92	2408.42
59	1	14	1698	010CT92	2405.44
59	1	13	1898	010CT92	2409.33
59	1	12	2195	010CT92	2415.59
59	1	11	2500	010CT92	2420.43
59	1	10	2800	010CT92	2421.90
59	1	09	3098	010CT92	2420.55
59	1	08	3402	010CT92	2419.33
59	1	03	4903	010CT92	2418.45
59	1	02	5104	010CT92	2420.77
59	1	01	5418	010CT92	2398.22
59	1	01	5418	010CT92	2399.13
61	1	34	10	020CT92	+0.91
62	1	34	9	020CT92	2399.96
62	1	34	0	020CT92	2302.15
62	1	35	0	020CT92	2301.30
62	1	33	23	020CT92	2307.01
62	1	32	49	020CT92	2300.13
62	1	31	74	020CT92	2304.98
62	1	30	99	020CT92	2312.12
62	1	29	125	020CT92	2318.85

X

1	06	4402	040CT92	A1341	2415.65	2415.65
1	05	4799	040CT92	A1340	2498.47	2498.47
1	04	5099	040CT92	A1339	2497.59	2497.59
63	1	03	5404	040CT92	2400.60	2400.60
63	1	02	5500	040CT92	2404.05	2404.05
63	1	01	5703	040CT92	2399.06	2399.06
63	1	01	5703	040CT92	2403.43	+4.37 2401.25
64	1	01	0	050CT92	2408.77	
64	1	01	0	050CT92	2407.98	
64	1	01	0	050CT92	2407.98	
64	1	01	0	050CT92	2406.55	-0.79 2408.38
64	1	01	0	050CT92	2413.83	
64	1	01	0	050CT92	2413.83	
64	1	01	0	050CT92	2412.28	
64	1	01	0	050CT92	2412.28	+5.45 2411.10
64	1	21	0	050CT92	2271.93	2271.93
64	1	36	10	050CT92	2312.54	2312.54
64	1	35	25	050CT92	2305.26	
64	1	35	25	050CT92	2317.79	+12.53 2311.53
64	1	34	49	050CT92	2316.76	2316.76
64	1	33	74	050CT92	2308.78	2308.78
64	1	32	98	050CT92	2320.56	2320.56
64	1	31	122	050CT92	2316.36	2316.36
64	1	30	148	050CT92	2316.89	2316.89
64	1	29	174	050CT92	2304.01	2304.01
64	1	28	198	050CT92	2298.92	2298.92
64	1	27	249	050CT92	2288.19	2288.19
64	1	26	297	050CT92	2282.75	2282.75
64	1	25	347	050CT92	2275.90	2275.90
64	1	24	399	050CT92	2276.80	2276.80
64	1	23	498	050CT92	2270.91	2270.91
64	1	22	593	050CT92	2273.30	2273.30
64	1	20	890	050CT92	2290.96	2290.96
64	1	19	795	050CT92	2305.85	2305.85
64	1	18	889	050CT92	2333.19	2333.19
64	1	17	996	050CT92	2346.84	2346.84
64	1	16	1098	050CT92	2366.82	2366.82
64	1	15	1198	050CT92	2372.55	2372.55
64	1	14	1297	050CT92	2386.81	2386.81
64	1	13	1397	050CT92	2387.51	2387.51
64	1	12	1598	050CT92	2405.11	2405.11
64	1	11	1798	050CT92	2388.17	2388.17
64	1	10	2000	050CT92	2416.06	2416.06
64	1	09	2197	050CT92	2410.85	2410.85
64	1	08	2499	050CT92	2421.09	2421.09
64	1	07	2797	050CT92	2415.03	2415.03
64	1	06	3099	050CT92	2421.38	2421.38
65	1	05	3401	050CT92	2417.92	2417.92
64	1	04	3704	050CT92	2422.09	2422.09
64	1	03	4002	050CT92	2410.41	2410.41
64	1	02	4301	050CT92	2415.20	2415.20
65	1	36	10	050CT92	2301.78	2301.78
65	1	35	25	050CT92	2300.07	
65	1	35	25	050CT92	2304.58	
65	1	34	48	050CT92	2305.90	
65	1	33	74	050CT92	2283.74	
65	1	32	98	050CT92	2286.53	
65	1	31	125	050CT92	2274.29	
65	1	30	148	050CT92	2282.55	
65	1	29	173	050CT92	2278.49	
65	1	28	200	050CT92	2277.78	
65	1	27	247	050CT92	2274.52	

X X

1	26	299	060CT92	080CT92	01432	2276.10	2276.10
1	25	349	060CT92	080CT92	01431	2271.99	2271.99
1	24	397	060CT92	080CT92	01430	2273.71	2273.71
1	23	498	060CT92	080CT92	01429	2270.71	2270.71
1	22	598	060CT92	080CT92	01428	2282.16	2282.16
1	21	698	060CT92	080CT92	01427	2290.08	2290.08
1	20	797	060CT92	080CT92	01426	2317.32	2317.32
1	19	898	060CT92	080CT92	01425	2336.57	2336.57
1	18	999	060CT92	080CT92	01424	2373.84	2373.84
1	17	1198	060CT92	080CT92	01423	2376.10	2376.10
1	16	1398	060CT92	080CT92	01422	2389.84	2389.84
1	15	1597	060CT92	080CT92	01421	2400.84	2400.84
1	14	1800	060CT92	080CT92	01420	2413.95	2413.95
1	13	2100	060CT92	080CT92	01419	2415.01	2415.01
1	12	2400	060CT92	080CT92	01418	2421.90	2421.90
1	11	2702	060CT92	080CT92	01417	2416.58	2416.58
1	10	3002	060CT92	080CT92	01416	2419.92	2419.92
1	9	3301	060CT92	080CT92	01415	2417.47	2417.47
1	8	3601	060CT92	080CT92	01414	2420.59	2420.59
1	7	3901	060CT92	080CT92	01413	2413.42	2413.42
1	6	4502	060CT92	080CT92	01412	2416.93	2416.93
1	5	4802	060CT92	080CT92	01411	2410.52	2410.52
1	4	5102	060CT92	080CT92	01410	2405.48	2405.48
1	3	5300	060CT92	080CT92	01409	2402.47	2402.47
1	2	5544	060CT92	080CT92	01408A	2403.12	2403.12
1	1	5544	060CT92	080CT92	01408B	2405.85	2405.85
1	36	11	080CT92	090CT92	01476	2331.46	2331.46
1	35	24	080CT92	090CT92	01475A	2278.40	2278.40
1	34	50	080CT92	090CT92	01474	2288.29	2288.29
1	33	73	080CT92	090CT92	01473	2279.80	2279.80
1	32	98	080CT92	090CT92	01472	2282.35	2282.35
1	31	128	080CT92	090CT92	01471	2305.54	2305.54
1	30	156	080CT92	090CT92	01470	2316.57	2316.57
1	29	176	080CT92	090CT92	01469	2313.65	2313.65
1	28	209	080CT92	090CT92	01468	2294.12	2294.12
1	27	249	080CT92	090CT92	01467	2275.36	2275.36
1	26	299	080CT92	090CT92	01466	2269.51	2269.51
1	25	349	080CT92	090CT92	01465	2282.98	2282.98
1	24	400	080CT92	090CT92	01464	2291.99	2291.99
1	23	500	080CT92	090CT92	01463	2312.41	2312.41
1	22	598	080CT92	090CT92	01462	2322.53	2322.53
1	21	699	080CT92	090CT92	01461	2337.08	2337.08
1	20	798	080CT92	090CT92	01460	2344.35	2344.35
1	19	899	080CT92	090CT92	01459	2354.26	2354.26
1	18	997	080CT92	090CT92	01458	2358.88	2358.88
1	17	1100	080CT92	090CT92	01457	2369.94	2369.94
1	16	1197	080CT92	090CT92	01456	2375.02	2375.02
1	15	1297	080CT92	090CT92	01455	2386.93	2386.93
1	14	1699	080CT92	090CT92	01454	2407.09	2407.09
1	13	1899	080CT92	090CT92	01453	2419.13	2419.13
1	12	2000	080CT92	090CT92	01452	2418.15	2418.15
1	11	2297	080CT92	090CT92	01451	2425.69	2425.69
1	10	2599	080CT92	090CT92	01450	2421.91	2421.91
1	9	3200	080CT92	090CT92	01449	2442.92	2442.92
1	8	3802	080CT92	090CT92	01448	2417.31	2417.31
1	7	3802	080CT92	100CT92	01447	2418.23	2418.23
1	6	4102	080CT92	100CT92	01446	2408.56	2408.56
1	5	4403	080CT92	100CT92	01445	2407.31	2407.31
1	4	4702	080CT92	100CT92	01444	2400.42	2400.42
1	3	4903	080CT92	100CT92	01443		

1	61	5117	080CT92	100CT92	A1443A	2399.68
66	1	6117	080CT92	100CT92	A1443B	2402.97
67	1	36	19	090CT92	A1612	2275.78
67	1	35	25	090CT92	100CT92	2272.50
67	1	34	49	090CT92	100CT92	2273.28
67	1	33	74	090CT92	100CT92	+0.78 2272.89
67	1	32	99	090CT92	100CT92	2278.43
67	1	31	125	090CT92	100CT92	2283.47
67	1	30	149	090CT92	100CT92	2283.05
67	1	29	173	090CT92	100CT92	2282.05
67	1	28	198	090CT92	100CT92	2282.05
67	1	27	247	090CT92	100CT92	2282.05
67	1	26	299	090CT92	100CT92	2282.05
67	1	25	348	090CT92	100CT92	2282.05
67	1	24	404	090CT92	100CT92	2282.05
67	1	23	499	090CT92	100CT92	2282.05
67	1	22	597	090CT92	100CT92	2282.05
67	1	21	697	090CT92	100CT92	2282.05
67	1	20	797	090CT92	100CT92	2282.05
67	1	19	898	090CT92	100CT92	2282.05
67	1	18	997	090CT92	100CT92	2282.05
67	1	17	1126	090CT92	100CT92	2282.05
67	1	16	1296	090CT92	100CT92	2282.05
67	1	15	1496	090CT92	100CT92	2282.05
67	1	14	1694	090CT92	100CT92	2282.05
67	1	13	1904	090CT92	100CT92	2282.05
67	1	12	2198	090CT92	100CT92	2282.05
67	1	11	2384	090CT92	100CT92	2282.05
67	1	10	2600	090CT92	100CT92	2282.05
67	1	9	2799	090CT92	100CT92	2282.05
67	1	8	3098	090CT92	100CT92	2282.05
67	1	7	3399	090CT92	100CT92	2282.05
67	1	6	3702	090CT92	100CT92	2282.05
67	1	5	4003	090CT92	100CT92	2282.05
67	1	4	4302	090CT92	100CT92	2282.05
67	1	3	4601	090CT92	100CT92	2282.05
67	1	2	4902	090CT92	100CT92	2282.05
67	1	1	5322	090CT92	100CT92	2282.05
68	1	34	25	090CT92	110CT92	2285.88
68	1	33	48	090CT92	110CT92	2272.17
68	1	32	74	090CT92	110CT92	2280.07
68	1	31	98	090CT92	110CT92	2282.58
68	1	30	123	090CT92	110CT92	2287.24
68	1	29	150	090CT92	110CT92	2300.79
68	1	28	179	090CT92	110CT92	2287.11
68	1	27	236	090CT92	110CT92	2273.50
68	1	26	298	090CT92	110CT92	2284.98
68	1	25	346	090CT92	110CT92	2299.46
68	1	24	397	090CT92	110CT92	2305.48
68	1	23	497	090CT92	110CT92	2311.32
68	1	22	596	090CT92	110CT92	2304.15
68	1	21	696	090CT92	110CT92	2336.74
68	1	20	798	090CT92	110CT92	2341.38
68	1	19	897	090CT92	110CT92	2354.89
68	1	18	996	090CT92	110CT92	2359.62

1	20	699	130CT92	A1702	2328.90
75	1	19	799	130CT92	2338.32
75	1	18	898	130CT92	2350.80
75	1	17	997	130CT92	2356.64
75	1	16	1098	130CT92	2365.60
75	1	12	1498	130CT92	2382.26
75	1	10	1697	130CT92	2403.42
75	1	09	1998	130CT92	2413.42
75	1	08	2297	130CT92	2413.42
75	1	07	2697	130CT92	2419.03
75	1	06	2899	130CT92	2422.55
75	1	05	3201	130CT92	2425.16
75	1	04	3502	130CT92	2422.13
75	1	03	3799	130CT92	2423.45
75	1	02	4101	130CT92	2419.48
75	1	01	4311	130CT92	2419.48
76	1	36	11	130CT92	2419.48
77	1	36	9	140CT92	2419.48
78	1	36	9	140CT92	2419.48
78	1	35	24	140CT92	2419.48
78	1	34	49	140CT92	2419.48
78	1	33	72	140CT92	2419.48
78	1	32	98	140CT92	2419.48
78	1	31	124	140CT92	2419.48
78	1	30	149	140CT92	2419.48
78	1	29	174	140CT92	2419.48
78	1	28	198	140CT92	2419.48
78	1	27	249	140CT92	2419.48
78	1	26	298	140CT92	2419.48
78	1	25	348	140CT92	2419.48
78	1	24	398	140CT92	2419.48
78	1	23	448	140CT92	2419.48
78	1	22	497	140CT92	2419.48
78	1	21	598	140CT92	2419.48
78	1	20	696	140CT92	2419.48
78	1	19	798	140CT92	2419.48
78	1	18	895	140CT92	2419.48
78	1	17	998	140CT92	2419.48
78	1	16	1097	140CT92	2419.48
78	1	14	1298	140CT92	2419.48
78	1	12	1498	140CT92	2419.48
78	1	10	1798	140CT92	2419.48
78	1	09	2097	140CT92	2419.48
78	1	08	2298	140CT92	2419.48
78	1	07	2599	140CT92	2419.48
78	1	06	2899	140CT92	2419.48
78	1	05	3200	140CT92	2419.48
78	1	04	3501	140CT92	2419.48
78	1	03	3801	140CT92	2419.48
78	1	02	4103	140CT92	2419.48
78	1	01	4432	140CT92	2419.48
78	1	01	4432	140CT92	2419.48
79	1	36	10	140CT92	2419.48
80	1	36	10	150CT92	2419.48
81	1	36	9	160CT92	2419.48
81	1	35	26	160CT92	2419.48
81	1	35	26	160CT92	2419.48
					+1.98
					2399.46
					-7.91
					2394.52
					2286.42
					2272.70
					2270.35
					2274.53
					2276.77

81	1 33	74	150CT92	A1786	2294.75
81	1 32	99	150CT92	A1785	2320.16
81	1 31	124	150CT92	A1784	2303.55
81	1 30	150	150CT92	A1783	2308.09
81	1 29	173	150CT92	A1782	2308.09
81	1 28	199	150CT92	A1781	2316.86
81	1 27	247	150CT92	A1780	2317.57
81	1 26	298	150CT92	A1779	2315.87
81	1 25	351	150CT92	A1778	2310.48
81	1 24	397	150CT92	A1777	2309.21
81	1 23	447	150CT92	A1776	2308.60
81	1 22	496	150CT92	A1775	2307.46
81	1 21	597	150CT92	A1774	2317.80
81	1 20	696	150CT92	A1773	2307.60
81	1 19	797	150CT92	A1772	2316.57
81	1 18	897	150CT92	A1771	2316.57
81	1 17	999	150CT92	A1770	2317.80
81	1 16	1100	150CT92	A1769	2307.60
81	1 14	1297	150CT92	A1768	2316.57
81	1 12	1497	150CT92	A1767	2326.49
81	1 10	1797	150CT92	A1766	2326.49
81	1 09	2100	150CT92	A1765	2332.56
81	1 08	2399	150CT92	A1764	2337.74
81	1 07	2700	150CT92	A1763	2348.85
81	1 06	3000	150CT92	A1762	2358.40
81	1 05	3299	150CT92	A1761	2380.75
81	1 04	3601	150CT92	A1760	2390.11
81	1 03	3901	150CT92	A1759	2405.78
81	1 02	4200	150CT92	A1758	2416.90
81	1 01	4501	150CT92	A1757	2418.35
81	1 01	4501	150CT92	A1756A	2422.95
82	1 36	10	150CT92	A1756B	2422.95
83	1 35	24	160CT92	A1755	2422.95
83	1 32	99	160CT92	A1754	2422.95
83	1 31	122	160CT92	A1753	2422.95
83	1 30	148	160CT92	A1752	2422.95
83	1 29	173	160CT92	A1751	2422.95
83	1 28	197	160CT92	A1750	2422.95
83	1 27	239	160CT92	A1749	2422.95
83	1 26	296	160CT92	A1748	2422.95
83	1 24	396	160CT92	A1747	2422.95
83	1 23	446	160CT92	A1746	2422.95
83	1 22	498	160CT92	A1745	2422.95
83	1 21	594	160CT92	A1744	2422.95
83	1 20	693	160CT92	A1743	2422.95
83	1 19	798	160CT92	A1742	2422.95
83	1 18	895	160CT92	A1741	2422.95
83	1 17	995	160CT92	A1740	2422.95
83	1 16	1094	160CT92	A1739	2422.95
83	1 14	1194	160CT92	A1738	2422.95
83	1 12	1398	160CT92	A1737	2422.95
83	1 10	1598	160CT92	A1736	2422.95
83	1 09	1794	160CT92	A1735	2422.95
83	1 08	1995	160CT92	A1734	2422.95
83	1 07	2194	160CT92	A1733	2422.95
83	1 06	2398	160CT92	A1732	2422.95
83	1 05	2595	160CT92	A1731	2422.95
83	1 04	2798	160CT92	A1730	2422.95

EX

				2423.81	2423.81
				2424.03	2424.03
				2422.52	2422.52
				2421.82	-0.70
				2288.63	2422.17
				2288.63	2286.63
				2281.62	2281.62
				2286.56	2286.56
				2282.94	2282.94
				2279.89	2279.89
				2282.98	+3.09
				2282.98	2281.44
				2285.04	2285.04
				2313.27	2313.27
				2314.34	2314.34
				2324.08	2324.08
				2355.44	2355.44
				2340.51	2340.51
				2344.66	2344.66
				2321.76	2321.76
				2314.25	2314.25
				2310.87	2310.87
				2305.96	2305.96
				2364.99	2364.99
				2307.50	2307.50
				2310.25	2310.25
				2317.47	2317.47
				2322.63	2322.63
				2332.52	2332.52
				2341.40	2341.40
				2350.39	2350.39
				2356.39	2356.39
				2368.76	2368.76
				2378.61	2378.61
				2396.27	2396.27
				2413.22	2413.22
				2412.77	2412.77
				2417.09	2417.09
				2426.36	2426.36
				2418.71	2418.71
				2269.52	2269.52

Flags: X: Observed titrator malfunction or operator error
EX: Data excluded from analysis

NOTE: Dilution factor of 1.00010 has been applied.

X

THE CARBON DIOXIDE PROJECT OF THE SCRIPPS INSTITUTION OF OCEANOGRAPHY
 GC92 CDRG SHIPBOARD ALK
 Bicarbonate Reference Material (STD A) Titration Data

5-OCT-94

ANALYSIS SAMPLE			ALK			
DATE	BOTTLE	TRIAL	FLAG	(UEQUIV/KG)	AVG ALK	STD DEV
18AUG92	A34	1		2308.68		
18AUG92	A34	2		2299.75		
18AUG92	A34	3		2306.72		
18AUG92	A42	1		2307.36		
18AUG92	A42	2		2305.31		
18AUG92	A42	3		2307.02		
19AUG92	A42	4	X	2313.92		
19AUG92	A42	5		2306.59		
19AUG92	A34	4	X	2319.77		
19AUG92	A34	5		2307.45		
25AUG92	A25	1		2306.34		
25AUG92	A25	2		2302.91		
25AUG92	A25	3		2298.68		
25AUG92	A25	4		2309.70		
25AUG92	A40	2		2312.72		
25AUG92	A40	3		2307.81		
25AUG92	A40	4		2298.47		
26AUG92	A44	1		2299.94		
26AUG92	A44	2		2308.20		
26AUG92	A44	3		2304.27		
26AUG92	A25	5		2299.74		
26AUG92	A30	1		2303.98		
26AUG92	A30	2		2303.64		
26AUG92	A30	3		2305.73		
26AUG92	A40	5		2307.43		
27AUG92	A30	4	X	2331.80		
27AUG92	A30	5	X	2314.02		
27AUG92	A44	4		2305.67		
27AUG92	A44	5		2301.64		
02SEP92	A5	1		2304.70		
02SEP92	A5	2		2296.75		
02SEP92	A5	3		2305.17		
02SEP92	A47	1		2304.01		
02SEP92	A47	2		2302.48		
02SEP92	A47	3		2304.44		
03SEP92	A47	4		2306.04		
03SEP92	A47	5		2302.76		
03SEP92	A5	4		2303.71		
03SEP92	A5	5		2305.69		
04SEP92	A17	1		2303.18		
04SEP92	A6	1		2302.70		
05SEP92	A17	2		2304.28		
05SEP92	A17	3		2304.09		
05SEP92	A6	2		2303.87		
05SEP92	A6	3		2304.91		
06SEP92	A17	4		2303.94		
06SEP92	A17	5		2304.44		
06SEP92	A6	4		2305.23		
06SEP92	A6	5		2301.94		
01OCT92	A2	1	X	2314.08		
01OCT92	A2	2	X	2315.84		
01OCT92	A45	1		2304.56		
01OCT92	A45	2		2304.88		

03OCT92	A2	3	X	2313.74
03OCT92	A2	4	X	2378.68
03OCT92	A2	5	X	2314.95
03OCT92	A45	3		2304.74
03OCT92	A45	5		2304.83
04OCT92	A46	1	EX	2379.80
04OCT92	A46	2		2299.31
04OCT92	A1	1		2300.76
04OCT92	A1	2		2302.97
05OCT92	A1	3		2302.68
05OCT92	A1	4		2301.61
05OCT92	A46	3		2298.96
05OCT92	A46	4		2305.45
06OCT92	A46	5		2306.50
06OCT92	A1	5		2293.04
09OCT92	A23	1		2305.80
09OCT92	A48	1		2304.79
10OCT92	A48	2		2306.38
10OCT92	A48	3		2302.55
10OCT92	A23	2		2302.13
10OCT92	A23	3		2304.64
11OCT92	A48	4		2306.07
11OCT92	A23	4		2299.93
14OCT92	A10	1		2305.20
14OCT92	A38	1		2306.25
15OCT92	A10	2		2303.13
15OCT92	A38	2		2304.30
16OCT92	A10	3		2302.17
16OCT92	A10	4		2305.50
16OCT92	A38	3		2305.63
16OCT92	A38	4		2302.87
17OCT92	A38	5		2306.74
17OCT92	A10	5		2306.67
				2304.24 2.77

FLAGS: X: Observed titrator malfunction or operator error

EX: Data excluded from analysis

NOTE: Dilution factor of 1.000170 has been applied.

THE CARBON DIOXIDE PROJECT OF THE SCRIPPS INSTITUTION OF OCEANOGRAPHY
 GC92 CDRG SHIPBOARD ALK
 Bicarbonate Reference Material (STD B) Titration Data

ANALYSIS DATE	SAMPLE BOTTLE	TRIAL FLAG	ALK (UEQUIV/KG)	Avg Alk	Std Dev
19AUG92	B2	1	2299.95		
19AUG92	B22	1	2300.10		
21AUG92	B22	2	2300.05		
21AUG92	B22	3	2295.82		
21AUG92	B2	2	2298.05		
21AUG92	B2	3	2300.24		
22AUG92	B22	4	2300.58		
22AUG92	B22	5	2300.78		
22AUG92	B2	4	2295.76		
22AUG92	B2	5	2298.19		
22AUG92	B26	1	2297.83		
22AUG92	B26	2	2297.14		
22AUG92	B44	1	2300.09		
22AUG92	B44	2	2299.96		
23AUG92	B44	3	2297.11		
23AUG92	B44	4	2297.03		
23AUG92	B26	3	2300.80		
23AUG92	B26	4	2296.17		
24AUG92	B26	5	2300.04		
24AUG92	B44	5	2298.01		
27AUG92	B7	1	2299.15		
27AUG92	B7	2	2299.91		
27AUG92	B25	1	2298.37		
27AUG92	B25	2	2300.06		
28AUG92	B25	3	2300.24		
28AUG92	B25	4	2300.18		
28AUG92	B7	3	2300.24		
28AUG92	B7	4	2297.40		
30AUG92	B7	5	2301.23		
30AUG92	B13	1	2302.43		
30AUG92	B25	5	2296.62		
30AUG92	B45	1	2297.38		
31AUG92	B45	2	2299.88		
31AUG92	B45	3	2299.05		
31AUG92	B13	2	2297.79		
31AUG92	B13	3	2299.69		
01SEP92	B13	4	2297.58		
01SEP92	B13	5	2298.87		
01SEP92	B45	4	2299.62		
01SEP92	B45	5	2296.65		
06SEP92	B9	1	2298.32		
06SEP92	B28	1	2298.29		
07SEP92	B28	2	2300.38		
07SEP92	B28	3	2297.29		
07SEP92	B9	2	2298.90		
07SEP92	B9	3	2298.86		
08SEP92	B9	4	2297.63		
08SEP92	B9	5	2299.64		
08SEP92	B19	1	2297.70		
08SEP92	B28	4	2299.06		
08SEP92	B28	5	2297.84		
08SEP92	B39	1	2295.12		
09SEP92	B39	2	2296.06		

09SEP92	B19	2	2294.54
11SEP92	B19	3	2298.03
11SEP92	B19	4	2298.52
11SEP92	B19	5	2299.57
11SEP92	B39	3	2296.81
11SEP92	B39	4	2297.80
11SEP92	B39	5	2295.52
06OCT92	B20	1	2293.25
06OCT92	B20	2	2291.57
06OCT92	B34	1	EX 2346.30
06OCT92	B34	2	2301.37
07OCT92	B34	4	2296.11
07OCT92	B20	4	2299.73
08OCT92	B34	5	2302.11
08OCT92	B20	5	2298.16
12OCT92	B4	1	2298.53
12OCT92	B4	2	2295.34
12OCT92	B4	3	2301.05
12OCT92	B46	1	2296.09
12OCT92	B46	2	2300.50
12OCT92	B46	3	2299.88
13OCT92	B46	4	2295.40
13OCT92	B4	4	2293.13
14OCT92	B4	5	2300.29
14OCT92	B46	5	2300.04
17OCT92	B10	1	2299.56
17OCT92	B16	1	2299.45
18OCT92	B16	2	2299.93
18OCT92	B16	3	2300.62
18OCT92	B10	2	2296.95
18OCT92	B10	3	2300.52
19OCT92	B10	4	2300.93
19OCT92	B10	5	2298.38
19OCT92	B16	4	2301.71
19OCT92	B16	5	2301.83
19OCT92	B36	1	2301.80
19OCT92	B40	1	2302.32
20OCT92	B36	2	2299.73
20OCT92	B40	2	2301.21 2298.68 2.15

FLAGS: X: Observed titrator malfunction or operator error

EX: Data excluded from analysis

NOTE: Dilution factor of 1.000170 has been applied.

THE CARBON DIOXIDE PROJECT OF THE SCRIPPS INSTITUTION OF OCEANOGRAPHY
 GC92 CDRG SHIPBOARD ALK
 Certified DIC Reference Material (No. 13) Titration Data

ANALYSIS DATE	SAMPLE BOTTLE	TRIAL	FLAG	ALK (UEQUIV/KG)	Avg Alk	STD Dev
19AUG92	1PM	1		2203.05		
19AUG92	220PM	1		2199.12		
21AUG92	13PM	1		2203.86		
21AUG92	33PM	1		2206.70		
22AUG92	231PM	1		2203.58		
22AUG92	436PM	1		2202.77		
23AUG92	4PM	1		2201.34		
23AUG92	170PM	1		2200.43		
24AUG92	486PM	1		2203.29		
24AUG92	478PM	1		2201.36		
26AUG92	9PM	1		2200.22		
26AUG92	52PM	1		2216.25		
27AUG92	356PM	1		2201.48		
27AUG92	356PM	2		2205.08		
27AUG92	443PM	1		2204.48		
27AUG92	443PM	2		2202.30		
28AUG92	452PM	1		2203.09		
28AUG92	487PM	1		2202.97		
31AUG92	121PM	1		2201.65		
31AUG92	320PM	1		2202.69		
01SEP92	44PM	1		2202.32		
01SEP92	380PM	1		2201.37		
02SEP92	165PM	1		2200.07		
02SEP92	209PM	1		2201.94		
03SEP92	122PM	2		2199.62		
03SEP92	274PM	1		2199.40		
03SEP92	274PM	2		2198.11		
05SEP92	438PM	1		2199.71		
05SEP92	425PM	1		2200.99		
06SEP92	97PM	1		2202.59		
06SEP92	472PM	1		2200.62		
07SEP92	182PM	1		2201.64		
07SEP92	193PM	1		2200.76		
08SEP92	298PM	1		2199.26		
08SEP92	226PM	1		2200.83		
10SEP92	7PM	1		2200.06		
10SEP92	150PM	1		2201.54		
11SEP92	232PM	1		2201.65		
11SEP92	232PM	2		2202.04		
11SEP92	445PM	1		2201.06		
01OCT92	294PM	1		2199.74		
03OCT92	353PM	1	X	2270.76		
04OCT92	148PM	1		2199.09		
04OCT92	290PM	1	EX	2279.33		
06OCT92	240PM	1	EX	2261.49		
06OCT92	250PM	2		2196.27		
06OCT92	296PM	2		2199.49		
06OCT92	407PM	1		2196.10		
07OCT92	264PM	1		2197.91		
07OCT92	264PM	2		2195.06		
07OCT92	264PM	3		2196.05		
07OCT92	387PM	1		2203.21		
07OCT92	387PM	2	EX	2237.63		

07OCT92	387PM	3	2198.53
08OCT92	67PM	1	2198.68
08OCT92	80PM	1	2203.34
08OCT92	80PM	2	2197.89
08OCT92	366PM	1	2199.45
08OCT92	366PM	2	2202.55
08OCT92	195PM	1	2197.57
08OCT92	195PM	2	2204.20
08OCT92	421PM	1	2202.55
08OCT92	421PM	2	2198.02
08OCT92	484PM	1	2202.47
09OCT92	281PM	1	2199.57
09OCT92	348PM	1	2201.94
10OCT92	253PM	1	2182.30
10OCT92	418PM	1	2203.38
11OCT92	107PM	1	2201.02
11OCT92	499PM	1	2203.02
12OCT92	64PM	1	2200.89
13OCT92	423PM	1	2202.98
13OCT92	446PM	1	2203.09
14OCT92	235PM	1	2202.90
14OCT92	385PM	1	2202.88
15OCT92	230PM	1	2202.48
15OCT92	317PM	1	2202.21
16OCT92	475PM	1	2201.40
16OCT92	500PM	1	2204.22
17OCT92	333PM	1	2198.38
17OCT92	360PM	1	2203.45
18OCT92	222PM	1	2203.10
19OCT92	54PM	1	2204.84
19OCT92	318PM	1	2203.58
			2201.26 2.29

FLAGS: X: Observed titrator malfunction or operator error

EX: Data excluded from analysis

NOTE: Dilution factor of 1.000170 has been applied.