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Technical Progress Report

Title: Oceanic CO₂ Measurements for the WOCE Hydrological Survey In the Pacific Ocean; Shipboard Alkalinity Analyses During 1991 and 1992

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Summary of Progress

The DOE Carbon Dioxide Science Team is contributing measurements of the carbon system in sea water on transects of the WOCE Hydrological Survey sponsored by the United States. This project is to provide measurements of titration alkalinity of sea water, an effort that is in addition to our collecting samples of sea water brought back to our shore laboratory and analyzed for dissolved inorganic carbon (DIC) and alkalinity. Our original proposal called for approximately 1200 analyses at sea in 1991 and 4400 in 1992. In preparation for measurements at sea, the project budget called for the construction of a dual potentiometric sea-going titration system.

We have carried out the construction of this titrator system and have participated on Leg 3 of the 1991 WOCE Expedition from Papeete, Tahiti to Honolulu, Hawaii, as planned. Mr. Guenther of our research group was on board ship between August 31 and October 1.

The titration system is of novel design in order to achieve at sea as close as possible the same high precision that we have previously achieved in the laboratory using gravimetric procedures. Two motor driven precision syringes dispense sea water volumetrically to two titration cells, each separately connected to a Dosimat acid dispenser. Each system is driven by a notebook computer that analyzes the full titration curve of sea water and calculates the alkalinity.

Construction of the titrator proceeded approximately on schedule, but we encountered difficulties with the combination electrodes used in the titrator cell after construction. These did not give identical readings for the two systems. Also we were obliged to make some corrections to the electrical system before the two systems functioned optimally together. We learned that our having a dual system was a great advantage in striving for quality assured data. We were not, however, able entirely to remove the discrepancy between the two systems before going to sea. At sea, using new electrodes, there was at first no discrepancy detectable when comparing standard reference samples of sea water, but later on one system drifted until, near the end of the cruise, it gave readings $3 \mu\text{mol kg}^{-1}$ higher than the other system, which remained stable. A sufficient number of

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standards were run that we are able to correct our data, but we suspect that we can achieve better results in the future, if we can find a different kind of electrode pair, particularly one with a reference electrode having a more stable liquid junction to the sea water sample.

A total of 736 titrations of sea water and bicarbonate reference materials were run. Owing to the restricted size of the ship, only two carbon system analysts were on board, Ed Peltzer from the Woods Hole (WHOI) Group directed by Catherine Goyet and Peter Guenther. Peltzer operated only the WHOI coulometric DIC analysis system and Guenther operated only our alkalinity titration system, because it was deemed impossible for one person to operate both systems simultaneously. Thus neither system could be operated around the clock. During the cruise about every fourth station was sampled for carbon, a spacing of 2° of latitude. On these stations each of the 36 Niskin bottles were sampled. At most stations, all Niskin bottles were analyzed for DIC and about 27 Niskins for alkalinity. A total of 700 Niskins were sampled from 21 stations, with 652 analyzed for DIC and 552 for alkalinity. Preliminary profiles were plotted immediately after completion of analyses at sea. These look reasonable, displaying smooth changes in alkalinity with depth. Work on finalizing the data is underway.

Two types of reference materials were analyzed for alkalinity at sea, interspersed with the analyses of sea water. The first consisted of bicarbonate in sodium chloride solutions prepared in our laboratory and of the same type used by us previously for over five years. These solutions were bottled in 800 ml vitreous quartz bottles and were analyzed normally three times each. The second type of reference material also consisted of bicarbonate in sodium chloride solutions, prepared by the DOE supported standards laboratory under the direction of Andrew Dickson. These solutions were bottled in 500 ml Pyrex bottles. Their primary function serves as DIC reference materials. These were usually analyzed twice for alkalinity after having been analyzed once for DIC with the coulometric system. For our materials, 25 bottles were titrated a total of 80 times. The standard deviation of an individual measurement was found to be $1.52 \mu\text{mol kg}^{-1}$. For the Dickson materials, 43 bottles were titrated a total of 80 times. The standard deviation of an individual measurement was calculated to be $2.02 \mu\text{mol kg}^{-1}$.

Summary of Plans for Next Year

We plan to participate in WOCE expeditions up to 110 days at sea in 1992 on legs as determined by the DOE Science Team. Since, under this grant, we will be measuring only alkalinity, DIC measurements will be coordinated with other participating laboratories. If it can be arranged, at least one leg will include measurements of CO_2 partial pressure in order to check on the ability of the thermodynamic relationships to calculate this quantity from DIC and alkalinity.

This year we were unable to provide a third person to assist in the running of the equipment and in collecting of samples for shore analysis. On Leg 3 Mr. Guenther was obliged to collect all such samples as well as carrying out all of the titrations. If we are to achieve the stated goal of analyzing 4400 samples next

year, it is imperative that a third person be included on each cruise. This year, funds were provided for a third berth, but there was not space on the ship. For next year this grant provides only partially for such a third berth, the cost of which must presumably be shared between the various participating organizations.

Publications

None as yet have been written.

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