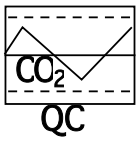

Copies of this certificate and others can be obtained at:

https://www.nodc.noaa.gov/ocads/oceans/Dickson_CRM/batches.html

University of California, San Diego
Scripps Institution of Oceanography
Marine Physical Laboratory
9500 Gilman Drive
La Jolla, CA 92093-0244

Certificate of Analysis

Reference material for oceanic CO_2 measurements

Batch 169 (Bottled August 4 , 2017)

This reference material consists of natural sea water sterilized by a combination of filtration, ultra-violet radiation and addition of mercuric chloride.

Analysis Results

The various procedures used for these analyses are detailed overleaf.

Salinity	33.518	
Total dissolved inorganic carbon		2063.31 ± 0.36 μmol·kg^{-1} (9; 9)
Total alkalinity		2207.03 ± 0.57 μmol·kg^{-1} (32; 16)

Phosphate	0.91	μmol·kg^{-1}
Silicate	6.3	μmol·kg^{-1}
Nitrite	0.00	μmol·kg^{-1}
Nitrate	8.7	μmol·kg^{-1}

The cited uncertainties represent the standard deviation. Figures in parentheses are the number of analyses made (total number of analyses; number of separate bottles analysed). The nutrient levels may have changed on storage, their stability has not been examined. CO_2 analyses were performed over a period of time to confirm that the batch is stable.

The 95% confidence limits for the means of the certified analyses are thus:

Total dissolved inorganic carbon	2063.31 ± 0.27 μmol·kg^{-1}
Total alkalinity	2207.03 ± 0.20 μmol·kg^{-1}

STORAGE: The bottles should be stored out of direct sunlight, and preferably at or below room temperature (25 °C). They should not be allowed to freeze!

Andrew Dickson

Andrew G. Dickson
November 14, 2017

Analytical Methods Used

Salinity

The salinity was determined by measuring its conductivity relative to IAPSO Standard Sea Water using a Guildline Autosal Model 8400 conductive salinometer. The procedure is described in an in-house technical manual of the Oceanographic Data Facility (ODF), Scripps Institution of Oceanography, entitled "Autosal Operating Procedures", dated 10-Dec-1993, revised 10-Jan-1994.

Total dissolved inorganic carbon

The total dissolved inorganic carbon was assayed in Dr. C. D. Keeling's laboratory at the Scripps Institution of Oceanography by the vacuum extraction/manometric procedure. The weighed sample is acidified with phosphoric acid; the CO_2 evolved is then extracted under vacuum and condensed in a trap cooled by liquid nitrogen. The water and CO_2 are separated from one another by sublimation and the CO_2 is transferred into an electronic constant-volume manometer [ECM]. There its pressure, volume and temperature are measured and the amount of CO_2 separated is computed from the virial equation of state.

Alkalinity

The total alkalinity was assayed by a two-stage, potentiometric, open-cell titration using coulometrically analyzed hydrochloric acid. A weighed sample of reference material is acidified to a pH between 3.5 and 4.0 with an aliquot of titrant. The solution is stirred for a period of time to allow the evolved CO_2 to escape. The titration is then continued to a pH of about 3.0 and the equivalence point evaluated from titration points in the pH region 3.0–3.5 using a non-linear least squares procedure that corrects for the reactions with sulfate and fluoride ions (Dickson, A. G., Afghan, J. D. & Anderson, G. C., 2003. Reference materials for oceanic CO_2 analysis: A method for the certification of total alkalinity. *Marine Chemistry* **80**, 185–197).

Nutrients

Nutrient levels were determined using a modified 4-channel autoanalyzer. The procedures are similar to those described in Gordon, L.I., J.C. Jennings, A.A. Ross, J.M. Krest (1993) "A Suggested Protocol for Continuous Flow Automated Analysis of Sea Water Nutrients (Phosphate, Nitrate, Nitrite, and Silicic Acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study", *WOCE Operations Manual*, WHP Office Report WHPO 91-1 (rev. Nov. 1994