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

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Certificate of Analysis

Reference material for oceanic CO₂ measurements

Batch 191 (Bottled 2/14/20)

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	33.316	
Total dissolved inorganic carbon		2051.40 ± 0.95 μmol·kg ⁻¹ (7; 7) **
Total alkalinity		2225.50 ± 0.85 μmol·kg ⁻¹ (41; 19)
Phosphate	0.43 μmol·kg ⁻¹	
Silicate	3.0 μmol·kg ⁻¹	
Nitrite	0.0 μmol·kg ⁻¹	
Nitrate	2.4 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. CO₂ 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	2051.40 ± 0.87 μmol·kg ⁻¹ **
Total alkalinity	2225.50 ± 0.27 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 G. Dickson
March 18, 2021

** Due to a mistake that occurred when preparing this batch (see note at bottom of next page), this calibrated value applies only to bottle numbers 1 to 1112. For bottles with larger numbers (n > 1112) an estimate of the total dissolved inorganic carbon can be obtained from the equation: C_T = 2051.4 + 0.068 * (n - 1112) μmol kg⁻¹ where n is the bottle number.

Analytical Methods Used

Salinity

The salinity was determined by measuring its conductivity relative to IAPSO Standard Sea Water using a Guildline Autosol 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 CO₂ evolved is then extracted under vacuum and condensed in a trap cooled by liquid nitrogen. The water and CO₂ are separated from one another by sublimation and the CO₂ is transferred into an electronic constant-volume manometer [ECM]. There its pressure, volume and temperature are measured and the amount of CO₂ 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 CO₂ 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 CO₂ 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

NOTE ABOUT THIS BATCH

When preparing this batch, the $p(\text{CO}_2)$ of the headspace was too high, and consequently later bottles in the fill sequence were contaminated with additional carbon. The extent of

this contamination was estimated from pH measurements in bottles from that region, together with a single total dissolved carbon measurement on bottle 1208.