

# **Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water.**

Prepared for the U. S. Department of Energy,  
Special Research Grant Program 89-7A:  
Global survey of carbon dioxide in the oceans.

**Version 2 — September 1994**  
**(version 2.1 is only available electronically)**

**Edited by**  
**Andrew G. Dickson & Catherine Goyet**

This document should be cited as:

DOE (1994) *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2*, A. G. Dickson & C. Goyet, eds., ORNL/CDIAC-74.



---

# Contents

## Acknowledgements

- 1 Introduction to the handbook
- 2 Solution chemistry of carbon dioxide in sea water
- 3 Quality assurance
- 4 Recommended standard operating procedures (SOPs)
  - SOP 1 Water sampling for the parameters of the oceanic carbon dioxide system
  - SOP 2 Determination of total dissolved inorganic carbon in sea water
  - SOP 3 Determination of total alkalinity in sea water
  - SOP 4 Determination of  $p(\text{CO}_2)$  in air that is in equilibrium with a discrete sample of sea water
  - SOP 5 Determination of  $p(\text{CO}_2)$  in air that is in equilibrium with a continuous stream of sea water
  - SOP 6 Determination of the pH of sea water using a glass / reference electrode cell
  - SOP 7 Determination of the pH of sea water using the indicator dye *m*-cresol purple
  - SOP 11 Gravimetric calibration of the volume of a gas loop using mercury
  - SOP 12 Gravimetric calibration of volume delivered using water
  - SOP 13 Gravimetric calibration of volume contained using water
  - SOP 14 Electronic calibration of the UIC Model 5011 coulometer
  - SOP 21 Applying air buoyancy corrections
  - SOP 22 Preparation of control charts
  - SOP 23 Statistical techniques used in quality assessment
  - SOP 24 Calculation of the fugacity of carbon dioxide in the pure gas or in air
- 5 Physical and thermodynamic data



---

## Acknowledgments

The procedures and advice contained in this handbook result from various meetings, conversations and written materials provided by the following persons; where a particular person contributed substantially to a particular procedure, the SOP number is identified after their name.

- Dr. Robert H. Byrne (7)  
Department of Marine Science  
University of South Florida  
140 Seventh Avenue South  
St. Petersburg, FL 33701-5016
- Dr. Douglas M. Campbell  
Division of Marine and Atmospheric Chemistry  
Rosenstiel School of Marine and Atmospheric Sciences  
University of Miami  
4600 Rickenbacker Causeway  
Miami, FL 33149-1098
- Dr. David W. Chipman (1, 2, 4)  
Lamont-Doherty Earth Observatory  
Columbia University  
Palisades, NY 10964
- Ms. Tonya D. Clayton (7)  
Department of Marine Science  
University of South Florida  
140 Seventh Avenue South  
St. Petersburg, FL 33701-5016
- Dr. Andrew G. Dickson (3, 11, 12, 13, 21, 22, 23, 24)  
Marine Physical Laboratory  
Scripps Institution of Oceanography  
University of California, San Diego  
9500 Gilman Drive  
La Jolla, CA 92093-0902
- Dr. Richard A. Feely (5)  
NOAA Environmental Research Laboratories  
Pacific Marine Environmental Laboratory  
7600 Sand Point Way, N.E.  
Seattle, WA 98115-0070
- Mr. Peter Guenther (1)  
Geological Research Division  
Scripps Institution of Oceanography  
University of California, San Diego  
9500 Gilman Drive  
La Jolla, CA 92093-0220

## Acknowledgements

---

- Dr. Catherine Goyet (2, 3)  
Department of Marine Chemistry and Geochemistry  
Woods Hole Oceanographic Institution  
Woods Hole, MA 02543
- Mr. Ken M. Johnson (2, 14)  
Oceanographic and Atmospheric Sciences Division  
Brookhaven National Laboratory  
Upton, NY 11973
- Dr. Frank J. Millero (6)  
Division of Marine and Atmospheric Chemistry  
Rosenstiel School of Marine and Atmospheric Sciences  
University of Miami  
4600 Rickenbacker Causeway  
Miami, FL 33149-1098
- Dr. Christopher Sabine  
Geology Department, Guyot Hall  
Princeton University  
Princeton, NJ 08544
- Dr. Doug Wallace  
Oceanographic and Atmospheric Sciences Division  
Brookhaven National Laboratory  
Upton, NY 11973
- Dr. Rik Wanninkhof (4, 5)  
Ocean Chemistry Department  
NOAA / AOML  
4301 Rickenbacker Causeway  
Miami, FL 33149
- Dr. Ray F. Weiss (5, 24)  
Geological Research Division  
Scripps Institution of Oceanography  
University of California, San Diego  
9500 Gilman Drive  
La Jolla, CA 92093-0220
- Mr. Kevin Wills (14)  
6023 Balsam Street  
Arvada, CO 80004
- Dr. Christopher D. Winn  
Department of Oceanography  
University of Hawaii  
1000 Pope Road  
Honolulu, HI 96822

Thanks are also due to the many people who have contacted me with information about errors contained in previous versions.