

Alkalinity and pH measurements

The analytical methodology used during the Prosopé cruise is that described in Copin-Montégut, 1993. Some little changes have been introduced : An automatic Metrohm burette 665 and a Radiometer pHmeter PHM93 were interfaced to a PC computer and were controlled by a Qbasic program. The composition of the TRIS buffer used to standardise the pH electrodes was that given by Dickson and Goyet (1994). The salinity of the TRIS buffer was 37.5. The dissociation constants for carbonic acid of Mehrbach *et al.*, (1973) corrected to the total hydrogen ion concentration scale (pH_T) were used instead of that proposed by Dickson and Millero (1987). The Mehrbach *et al* constants were first corrected to the SWS pH scale using the equation calculated by Dickson and Millero (1987) and then corrected to the pH_T scale (Roy *et al.*, 1993).

References

- Copin-Montégut C., 1993. -Alkalinity and carbon budgets in the Mediterranean, Global biogeochemical cycles, 7, 915-925.
- Dickson A.G. and C. Goyet, 1994. -Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water, DOE, version 2, ORNL/CDIAC-74.
- Dickson A.G. and F.J. Millero, 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. Deep-Sea Research, 34, 1733-1743.
- Mehrbach C. , C.H. Culberson, J.E. Hawley, and R.M. Pytkowicz, 1973. -Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnology and Oceanography, 18, 897-907.
- Roy R.N., L.N. Roy, K.M. Vogel, C. Porter Moore, T Pearson, C.E. Good, F.J. Millero, D.M. Campbell, 1993. -The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. Marine Chemistry, 44, 249-267.

In the middle of each set of measurements, the pH and alkalinity of certified reference material (Batch #47, bottled on January 26, 1999 supplied by Dr A.G. Dickson of Scripps Institution of Oceanography, USA) were measured. The certified values of alkalinity and total dissolved inorganic carbon for this batch of salinity 33.716 are :

$$TA = 2227.93 \pm 0.26 \mu\text{mole kg}^{-1}$$

$$DIC = 2006.61 \pm 0.42 \mu\text{mole kg}^{-1}$$

The pH_T at 25°C of this material, calculated using the Mehrbach *et al.* constants, is 7.926.

The values obtained for this reference material during the Prosopé cruise are in the following table :

Stations	TA $\mu\text{mole kg}^{-1}$	DIC * $\mu\text{mole kg}^{-1}$	pH at 25°C
1	2227.7	2010.0	7.919
3	2227.2	2008.0	7.922
4	2227.0	2008.6	7.920
5	2227.5	2011.0	7.916
MIO	2229.1	2011.9	7.917
7	2228.2	2011.4	7.917
8 & 9	2227.6	2010.7	7.917
DYF	2227.7	2010.0	7.919

* calculated using the Mehrbach *et al.* constants

Data arrangements :

1st column : Name of the station

2nd column : Number of the CTD

3rd column : Depth

4th column : Salinity

5th column : Alkalinity in micromole kg⁻¹

6th column : pH at 25°C in the pH_T scale

The depth values are rounded off and the salinity values are not corrected. The right values are in the bottle file (prosope.btl).