Along the MOC$^2$Equatorial 2010, several samples of water masses were taken from the whole water column. Samples of $A_T$, pH, $O_2$ and $CO_3^{2-}$ were analysed on board, on the chemistry lab of the Spanish R/V Hespérides, while $C_T$ samples were measured after in the CO$_2$ lab of Instituto de Investigaciónes Mariñas (IIM-CSIC) in Vigo (Spain).

In the next table the number of measured samples per each variable is shown. In addition, the number of stations from the total of 109 where these samples were collected are also shown.

<table>
<thead>
<tr>
<th></th>
<th>$O_2$</th>
<th>pH</th>
<th>$CO_3^{2-}$</th>
<th>$A_T$</th>
<th>$C_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nº muestras</td>
<td>1614</td>
<td>1559</td>
<td>687</td>
<td>958</td>
<td>50</td>
</tr>
<tr>
<td>Estaciones</td>
<td>72</td>
<td>70</td>
<td>30</td>
<td>43</td>
<td>16</td>
</tr>
</tbody>
</table>

**Winkler Oxygen ($O_2$)**

With the main purpose of calibrating the $O_2$ sensor of CTD, samples of $O_2$ was taken in all the stations at twenty four levels of depth in the 7.5ºN section of MOC$^2$Equatorial 2010. The $O_2$ samples were analysed following the widely applied Winkler method (1888).

The $O_2$ samples were always the first in being taken from the Niskin bottles of the rosette. Samples were collected in calibrated flasks (~250 mL) with a PVC pipe avoiding the bubble formation. The sample fixation (precipitation) were done by adding 0.6 mL of manganous salt ($MnCl_2 \cdot 4H_2O$) and 0.6 mL of alkali-iodide solution (NaOH + NaI). These samples have to be stored at darkness at least 24 hours before being measured. Then, 1 ml of sulphuric acid is added to dissolve the precipitate and to titrate the $O_2$ sample with thiosulfate 0.01N using a automatic 5ml burette “Titandro Metrohm”. Taking into account the stoichiometry and the used volume of thiosulfate, the $O_2$ concentration is obtained in $\mu$mol kg$^{-1}$.

The $O_2$ concentration distribution of 7.5ºN section is represented using the Ocean Data View program (ODV) (Schlitzer, R., 2011).
pH

Seawater pH samples were taken at twenty four levels of all stations along section 7.5ºN of MOC² Equatorial cruise. The pH measurements were made using the spectrophotometric method described in Clayton and Byrne (1993). This method consists of adding 75 µl of m-cresol purple (mCP) to the seawater sample and measuring the absorbance of the sample at three wavelengths, i.e., λ_{HI} = 434 nm, λ_{I} = 578 nm and λ_{non-abs} = 730 nm. The reaction of interest at seawater pH is the second dissociation HI⁻(aq) = H⁺(aq) + I²⁻(aq) in which I is the indicator. Then the total hydrogen ion concentration can be determined by pH = pK₂ + log₁₀[I²⁻]/[HI⁻].

pH samples were taken directly from the Niskin bottles into special optical glass spectrophotometric Hellma cells of 28 mL of volume and 100 mm of path length. These cells were carefully stored around one hour before the analysis in a thermostatic bath in which the temperature was controlled at 25.0ºC. Absorbance measurements were performed with the Shimadzu UV 2401 PC spectrophotometer on board the R/V Hespérides. The pH values were given following the equations described in Dickson et al. (2007), who includes the correction due to the difference between seawater and the indicator acidity (ΔR). Apart from that, the effect of the impurities of the indicator described in Yao et al. (2007) was also applied, using the following equation to obtain the corrected pH data in seawater scale at 25ºC:
Taking into account these pH data, the complete pH profile of the 7.5ºN section was plotted using ODV, as it is shown in the next graph.

Alkalinity (A_T)

Samples of A_T were taken during MOC² in almost the half of the total stations. In order to analyse these A_T samples on board, the water was transferred directly from the Niskin bottle to 600 mL borosilicate glass bottles and stored for twenty-four hours before the analyses. Measurements of A_T were done by a one endpoint method using an automatic potentiometric titrator (Titrand 801 Metrohm) with a combined glass electrode (Perez and Fraga, 1987). A Knudsen pipette (~250 mL) was used to transfer the samples into an open Erlenmeyer flask in which the potentiometric titration was carried out with HCl (0.1 M). The final volume of titration was determined by means of two pH endpoints very close to one another, i.e., 4.45 and 4.42 (Mintrop et al., 2000). These AT measurements were done in 12 sets of analysis.

In order to estimate the accuracy of the A_T method, alkalinity measurements of certified reference material (CRM) of CO₂ from batch 99 provided by Dr. Andrew Dickson have been
analysed. And in addition, an extra calibration (substandard) was made by using a closed container of 50 L filled with open ocean surface water.

The distribution of $A_T$ concentrations in $\mu$mol-Kg$^{-1}$ of the 7.5ºN section is shown in the next plot which was drawing using ODV.

![7.5ºN $A_T$ distribution in the MOC² Equatorial cruise.](image)

**Total inorganic carbon ($C_T$)**

Along MOC² 50 discrete samples of $C_T$ were taken in the water column to be measured in the CO$_2$ lab of IIM in Vigo (Spain) using a SOMMA (Single-Operator Multiparameter Metabolic Analyzers) system connected to a model CM101_093 coulometer (UIC,INC, Joliet, ILLINOIS, USA). $C_T$ samples were collected in 600 mL borosilicate glass bottles avoiding the formation of bubbles. To keep the samples free of fouling formation, 300 $\mu$L of de HgCl$_2$ (sat) were added into the bottles and conserving in darkness. The analysis consists on acidifying an aliquot of 20 mL with H$_3$PO$_4$ in a glass stripping chamber. Then, the resulting CO$_2$ gas is carried in the equipment by a free-CO$_2$ gas (N$_2$) into a coulometric cell, in which the coulometrical trititation is performed (Johnson et al., 1993).
In order to estimate the accuracy of the $A_T$ method, alkalinity measurements of certified reference material (CRM) of CO$_2$ from batch 99 provided by Dr. Andrew Dickson have been analysed. And in addition, an extra calibration (substandard) was made by using a closed container of 50 L filled with open ocean surface water.

$C_T$ measurements of certified reference material (CRM) of CO$_2$ from batch 100 provided by Dr. Andrew Dickson have been analysed in every $C_T$-analysis session in order to check the accuracy of the measurements.

The good agreement between these measured $C_T$ and those calculated from $A_T$ and pH using the inorganic carbon system thermodynamic equations and the acid constants from Mehrbach et al. (1973) fitted by Dickson & Millero (1987) is shown in the next graph, in which calculated $C_T$ fits well with measured $C_T$ ($R^2=0.998$).

![Graph showing the linear adjustment between calculated and measured $C_T$.](image)

Due to this high correlation, the calculated $C_T$ profile is shown in the next graph for the 7.5°N section.
7.5°N calculated $C_T$ distribution in the MOC² Equatorial cruise.

**Ion Carbonate (CO$_3^{2-}$)**

Natural seawater samples of CO$_3^{2-}$ were collected from the whole water column along thirty stations in MOC² at 24 levels of depth. These CO$_3^{2-}$ samples were analysed on board the R/V Hespérides following the spectrophotometric method described in Byrne and Yao (2008). This method consists on the addition of 225 µL of stock solution of PbCl$_2$ (1.1 mM) to the seawater sample in order for this Pb$^{2+}$ to react with the dissolved CO$_3^{2-}$ of the sample obtaining the complex PbCO$_3$. The [CO$_3^{2-}$] is calculated in terms of UV absorbance ratios using the next equation (eq. 5 of Byrne and Yao, 2008).

$$-\log\text{[CO}_3^{2-}\text{]}_T = \log\text{CO}_3 \beta_1 + \log\left(\frac{R-e_1}{e_2-R-e_3}\right)$$

Where $R = \left(\frac{\lambda_2-\lambda_3}{\lambda_1-\lambda_3}\right)$, in which $\lambda_1$ (234 nm) is the UV absorbance wavelengths at the isobestic point of PbCO$_3$, $\lambda_2$ (250 nm) is mean value of wavelengths presented high absorbance variation and $\lambda_3$ (350 nm) a non-absorbing wavelength to correct the sample manipulation.

Seawater was transferred directly from Niskin bottles into cylindrical quartz Perkin Elmer cells of 28 mL of volume and 100 mm of path length. These cells were carefully stored in a thermostatic bath at 25°C at least one hour before the analysis. Absorbance measurements
were performed with a Shimadzu UV 2401 PC spectrophotometer on board the R/V Hespérides.

The distribution of \( \text{CO}_3^{2-} \) along the 7.5ºN is plotted in the next graph using the ODV program.

![Graph showing the distribution of CO\(_3\)\(^{2-}\) along 7.5ºN](image)

7.5ºN \( \text{CO}_3^{2-} \) distribution in the MOC\(^2\) Equatorial cruise.

References


