

## 1. OceanSITES site information

**OceanSITES SITE code:** EuroSITES

**Institution:** Instituto Canario de Ciencias Marinas

**References:** <http://iccmoceanography.com/> , <http://www.estoc.es/en/> ,  
<http://www.eurosites.info> , <http://www.oceansites.org> , <http://www.coriolis.eu.org>

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**Source:** water column observation (sampling)

**Area:** eastern subtropical North Atlantic (Canary Islands)

**Southern most Latitude:** 29° N

**Southern most Latitude:** 29° 15' N

**Western most Longitude:** 016° W

**Eastern most Longitude:** 015° W

## 2. OceanSITES platform and dataset information

**OceanSITES SITE code:** The European Station for Time Series in the Ocean, ESTOC

**Dataset Id:**

**Data type:** OceanSITES time- series data from 1994 to present

**Data title:** Oceanographic data from The European Station for Time Series in the Ocean, ESTOC

**Dataset Summary:** The samples were collected using CTD + water sampler always that both were available from ship infrastructure. Nansen bottles fixed in the oceanographic cable were the alternative to the water sampler. 24 depth levels to bottom were used and distributed as surface, 10, 25, 50, 75, 100, 125, 150, 200, 300, 400, 600, 800, 1000, 1100, 1200, 1300, 1500, 1800, 2000, 2500, 2800, 3000, 3500 m. Reversed thermometers (protected and unprotected) in the beginning, as well as electronic reversed thermometers and pressure sensors have been used to determine the real depths or validating the CTD + water sampler records. The temperature and salinity data (from January 1994 to July 1995) were acquired by discrete sampling using reversing thermometers and salinity samples, which were analyzed on a Guideline salinometer. The other CTD measurements were taken using different instruments at ESTOC during the survey period: a self-contained CTD probe from SIS, and CTD probes from IDRONAUT, Seabird and Neil-Brown. The TS-profiles were individually quality controlled following the WOCE protocols.

Samples were collected immediately after the bottles were on board from each depth. The sampling sequence was as follows:

1.) Oxygen: was taken in glass bottles of about 125 ml of volume which were previously cleaned and washed with HCl acid and was fixed at once; then it was kept for at least six hours according to WOCE regulations and finally it was analysed at the laboratory on board the ship.

2.) Nutrients: were taken in polypropylene bottles which were previously cleaned and washed with HCl acid and were completely dry. Samples were immediately frozen at -20°C, analysing them as soon as possible after arrival at the laboratory. Freezing the samples is a common practice; it does not or only in a non-significant way affect the nitrate+nitrite and the phosphate values (by a slight decrease) and is not noticeable in the silicate values (Kremling and Wenck,1986; McDonald and McLunghlin, 1982).

3.) Aluminium: the samples are kept in polypropylen bottles previously cleaned, washed with HCl and dried, and wrapped in plastic bags (each bottle individually) to avoid any

contact with other ship materials. They are taken with gloves and each bottle is rinsed at least three times with water from the respective level, being subsequently frozen at -20°C to be transferred to the laboratory, where they are analysed according to the method following (Hernández-Brito et al., 1994a).

4.) Alkalinity and pH samples were taken in glass bottles, each bottle is rinsed with water from the respective level and the samples are fixed consequently.

5.) Gelbstoff: water was taken in dark glass bottles which were previously cleaned and washed with HCl acid. The samples were analysed within 3 hours of having taken them by spectrofluorometry.

6.) Salinity: samples were taken in dark glass bottles which were previously cleaned and washed with HCl acid. Then, they were kept in boxes to protect them from light till analysis on land.

6.) Chlorophyll: samples of one liter of water were taken. The chlorophyll samples were filtered immediately and the filters were frozen subsequently at -20°C. Their analyses take place at the ICCM laboratory in land.

All samples were taken using the procedures established in the WOCE Operations Manual, WHP Office Report WHPO 91-1/WOCE Report No.68/91.

## **Analysis**

Dissolved Oxygen: The samples were analysed using the method described in the WOCE Operations Manual, WHP Office Report No. 68/91; the final titration point was detected using a Metrohm Dosimat Oxygen Auto-Titrator Analyser.

## Nutrients

The nutrients determination was performed with a segmented continuous-flow autoanalyser, a Skalar® San Plus System (ICCM).

Nitrate+Nitrite: The automated procedure for the determination of nitrate and nitrite is based on the cadmium reduction method; the sample is passed through a column containing granulated copper-cadmium to reduce the nitrate to nitrite (Wood et al.,1967), using ammonium chloride as pH controller and complexer of the cadmium cations formed (Strickland and Parsons, 1972). The optimal column preparation conditions are described by several authors (Nydahl, 1976; Garside, 1993).

Phosphate: Orthophosphate concentration is understood as the concentration of reactive phosphate (Riley and Skirpow,1975) and according to Koroleff (1983a) is a synonym of “dissolved inorganic phosphate”. The automated procedure for the determination of phosphate is based on the following reaction: ammonium molybdate and potassium antimony tartrate react in an acidic medium with diluted solution of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-coloured complex, ascorbic acid. The complex is measured at 880nm. The basic methodology for this anion determination is given by Murphy and Riley (1962); the used methodology is the one adapted by Strickland and Parsons (1972).

Silicate: The determination of the soluble silicon compounds in natural waters is based on the formation of the yellow coloured silicomolybdic acid; the sample is acidified and mixed with an ammonium molybdate solution forming molybdosilicic acid. This acid is reduced with ascorbic acid to a blue dye, which is measured at 810nm. Oxalic acid is added to avoid phosphate interference. The used method is described in Koroleff (1983b).

Aluminium: The method of analysis is based on complexation of aluminum with 1,2-dihydroxyanthraquinone-3-sulphonic acid (DASA) and measurement of the reduction current of this complex using high speed cathodic stripping voltametry (HSCSV). Samples were prepared in Teflon cups of polarographic cell, containing 10 ml of water,  $2 \cdot 10^{-6}$  M DASA and 0.01 M BES. The adsorption potential (-0.9 V/Ag/AgCl) was applied to the working electrode, while the solution was stirred. After 40s accumulation time, the stirring was stopped and 5s were allowed for the solution to become quiescent. The scanning was started at -0.9 V and terminated at -1.4 V. The scanning is made using staircase modulation with a scan rate of 30 V/s and a pulse height of 5 mV. The DASA-Al peak appears at ca. -1.25 V. A standard addition procedure is used to quantify the aluminium concentration of the sample. The electrochemical system used has been designed to measure the instantaneous currents at short times with a low noise level (Hernandez-Brito et al., 1994b). Thus, the analytical time required for each sample is substantially reduced. A PAR-303A electrochemical cell with hanging mercury drop electrode (HMDE) was connected to a locally produced computer-controlled potentiostat.

Experimental pH: The pH in total scale (moles kg sol<sup>-1</sup>) was measured following the spectrophotometric technique of Clayton and Byrne (1993) using the m-cresol purple indicator (DOE, 1994). The pH measures were done in a Hewlett Packard Diode Array spectrophotometer, in a 25°C-thermostated 1-cm flow-cell by using a Peltier system. Using a stopped-flow protocol, the seawater was analysed for a blank determination at 730 nm, 578 nm and 434 nm. The flow was restarted and the indicator injection valve switched on to inject 10 µl dye through a mixing coil (2 m). Three photometric measurements were carried out for each injection in order to remove any dye effect on the seawater pH measurement. Repeated seawater measurements of different CRMs samples (n = 54) gave a weighted standard deviation of  $\pm 0.002$  pH units.

Total alkalinity: Total alkalinity of seawater ( $A_T$ ) was determined by titration with HCl until carbonic acid end point using two potentiometric systems (Mintrop et al., 2000). The titration systems consist of a titrator type Titrino 702SM (Metrohm, Herisau, Switzerland) and a Titrino 719S, respectively, both interfaced to personal computers. All measurements were made in thermostated plastic cells provided by Frank J. Millero (Rosenstiel School of Atmospheric and Marine Science (RSMAS), Miami, Florida, USA). The titration was performed by adding HCl to the seawater past the carbonic acid end point. A computer program was used to run the titration, record the volume of the acid added and the EMF readings of the electrodes. The HCl solution (25 l, 0.25 M) was made up from concentrated analytical grade HCl (Merck®, Darmstadt, Germany) in 0.45 M NaCl, in order to yield an ionic strength similar to open ocean seawater. The acid was standardized by titrating weighed amounts of Na<sub>2</sub>CO<sub>3</sub> dissolved in 0.7 M NaCl solutions. The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point,  $\text{pH}_{\text{equiv}} = 4.5$ , according to the exact definition of total alkalinity (Dickson, 1981). The precision of the fit (*s*-value) is better than  $0.4 \mu\text{mol kg}^{-1}$  for the samples analyzed. The performance of the titration systems ( $\pm 2 \mu\text{mol kg}^{-1}$ ) has been monitored by titrating different batches of CRMs (#42) that have known  $C_T$  and  $A_T$ .

Fugacity of CO<sub>2</sub>: Fugacity of carbon dioxide ( $f_{\text{CO}_2}$ ) in air and in surface seawater is determined with a flowing system similar to the one designed by Wanninkhof and

Thoning (1993) and developed by Frank J. Millero's group at the University of Miami. The equilibrator used is based on the design described by Weiss (1981). The concentration of CO<sub>2</sub> in the air and in the equilibrated air sample is measured with a differential, non-dispersive, infrared gas analyser supplied by LI-COR (LI-6262 CO<sub>2</sub>/H<sub>2</sub>O Analyser). The samples are measured wet and the signal corrected for water vapour using the water channel of the LI-COR. The instrument is operated in the absolute mode and gathers CO<sub>2</sub> concentrations directly from the instrument. The LICOR analyses the concentration of CO<sub>2</sub> in the instrument every 6 s, averages these values over a 1-min interval, and records them. Atmospheric air is pumped at the bow of the ship and measured every hour. The system was calibrated by measuring two different standard gases with mixing ratios of 348.55 and 520.83 ppm CO<sub>2</sub> in air. These calibrated standards were provided by NOAA Institution and they are traceable to the WMO (World Meteorology Organisation) scale. Our system has a precision of less than 1 µatm and is thought to be accurate, relative to the standard gases to 2 µatm. Fugacity of CO<sub>2</sub> in the seawater was calculated from the measured  $x_{CO_2}$  (mole fraction of CO<sub>2</sub> gas corrected to dry air and to the pressure of 1 atm).

Yellow Substance: The values were obtained using the methodology described by Determan et al. (1994, 1996). The samples were measured with a spectrofluorometer SHIMADZU RF-1501 at an excitation wavelength of 341 nm and the intensities taken at emission wavelength between 350 and 500 nm. Gelbstoff fluorescence is derived from the emission spectra and obtained in Raman units.

Phytoplankton pigments: Pigments were measured using fluorimetric analysis, following the methodology described by Welschmeyer (1994). The determination was achieved using a fluorometer TURNER 10-AU-000.

Salinity: Samples were measured with a salinometer, model Autosal 8400a, whose measurement range was between 0.005-42 (psu), with an accuracy of ±0.003, according to the manufacturer. It was calibrated following the manufacturer's information and standardizing it with IAPSO Standard Seawater. Salinity values were calculated as practical salinity according to Unesco (1978, 1984).