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HYDROGRAPHY AND VELOCITY MEASUREMENTS OFFSHORE FROM THE IBERIAN PENINSULA

BORD-EST

DATA REPORT - VOLUME 2

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1.4 Calibration of dissolved oxygen

The water samples were analysed according to the Winkler method and using a Methrom titroprocessor. Figure 13 showing the series of Winkler values at 3000 m, 4000 m and 4500 m, illustrates the variability of oxygen content at deep levels in the BORD-EST 3 region. These values may be regarded as uncertain by about 0.03 ml/l.

The procedure followed to calibrate the Beckman sensor from these sample values is similar to that used for the BORD-EST 2 cruise and described in Volume 1 of the BORD-EST data reports. It is basically that of Millard (1982) with the modification that the residuals from Millard's procedure can be eliminated by further adjustment of a five degree polynomial in pressure.

The algorithm is the following :

$$OXYC(ml/l) = soc \times OC \times OXSAT \times \exp \{ ozc \times [ozc1 \times T + ozc2(OT - T)] + ozcp \times P \} \quad (1)$$

where :

OC is the Beckman oxygen current,

OT is the Beckman sensor temperature,

P is the calibrated NBIS pressure,

T is the calibrated NBIS temperature,

soc is the oxygen current slope factor,

ozc is the temperature correction factor,

ozc1 equals 1 and *ozc2* is the weight factor of the Beckman sensor temperature,

ozcp is the pressure correction factor,

OXSAT is the oxygen saturation value (Weiss, 1970).

The above expression is linearized by taking its natural logarithm and the parameters *soc*, *ozc*, *ozc2* and *ozcp* determined through a linear least square regression. Calibration of the down profiles utilizes values of *OC*, *OT* and *T* averaged over intervals of thickness 15 db centered at the levels (calibrated pressure) where the samples were taken on the up-profiles. The whole set of stations had to be subdivided into several stations and groups of stations to apply this procedure. Table 3 gives, for each group, the resulting standard deviations of residuals, in the total water column, and below 2000 m.

Station or groups of stations	Standard deviation of residuals			
	Surface to bottom	2000 m to bottom	After 5° polynomial	
			Surface-bottom	2000 m-bottom
1	.113	.049	.040	.044
2-3	.082	.033		
4-10	.054	.037	.042	.038
11	.076	.064	.053	.028
12	.097			
13	.071	.059		
14-24	.065	.048	.059	.041
25	.067	.028		
26	.038	.035		
27-34	.054	.035		
35	.031			
36	.017			
37-38	.060	.018		
39-40	.044	.042	.034	.021
41-47	.056	.046	.051	.038
48-57	.069	.036	.064	.038
58	.046	.035		
59	.052	.064		

Table 3

On carrying out the regression on these station groups a weight of 9 was given to the samples below 3500 m to compensate for the less numerous samples in this layer, due to the choice of vertical sampling by the rosette and the presence of many shallow stations. Figure 14a shows, as an example, the residuals after application of Millard's (1982) procedure to the station group 14 to 23. A pressure dependent bias stands out on this figure, which is negative between 300 m and 1000 m and positive elsewhere. This misfit was reduced by fitting a 5 degree polynomial to these residuals and this led to the final residuals displayed on figure 14b. The improvement in terms of r.m.s. differences may be seen in table 3. This table indicates which station groups were run through this second calibration step which produced final standard deviations of residuals

around 0.04 ml/l below 2000 m.

The deep oxygen profiles ($p > 3000$ db) of stations 5 and 6 are reported on figures 15a,b for comparison with the two neighbouring ATLANTIS II stations. There is a good agreement between BORD-EST station 5 and ATLANTIS II station 93 which are distant from one another by less than 8 NM, but higher differences between the other station pairs. This could be indicative of horizontal gradients, but the poor adjustment of the continuous BE6 profile to some Winkler values (at 4000 db and 4500 db) also contributes to these differences. Also, the ATLANTIS II reported points were themselves extracted from calibrated continuous profiles, and on the whole, the differences are compatible with a 0.04 ml/l uncertainty on each data set.

1.5 The nutrients

The concentration of nitrate plus nitrite, phosphate, and silicate were determined on board immediately after sampling, using Technicon autoanalyzers with the following methods :

The nitrate was reduced to nitrite in a *Cd/Cu* column and it was determined with sulphanilamide and naphthylethylendiamine. The buffer solution in the reduction was prepared with citric acid and sodium citrate according to Mourino and Fraga (1985).

The phosphate was obtained from its reduction with molybdate in acid solution and reduction with ascorbic acid, as have reported Hansen and Grasshoff (1983).

The silicate concentration was obtained by reaction with molybdate according to the Hansen and Grasshoff (1983) method.

The standard for the analysis was a solution of KNO_3 , KH_2PO_4 and F_6SiNa_2 prepared in desionized water and preserved in refrigerator at 4°C.

Sub-standards were prepared by dilution in a seawater poor in nutrient salts. The nutrient salts concentration in poor seawater was determined and added to values of sub-standards.

Samples, in duplicate, of sub-standard and poor seawater were placed in the autoanalyzer system before and after each series of station samples.

The errors were estimated on the basis of the sub-standards and seawater signals. The confidence interval may be estimated to $\pm 0.04 \mu M$ for the nitrate plus nitrite, $\pm 0.01 \mu M$ for phosphate and $\pm 0.1 \mu M$ for silicate.

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