

PROSOPE

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Total organic carbon determined during Prosopé cruise

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Materials and Methods

Field sampling

Discrete seawater samples were collected by using a Seabird SBE 9 rosette sampler equipped with 24 12 dm³ Niskin bottles from the *RV Thalassa* at a series of stations. At the beginning of the cruise, Niskin bottles were cleaned with HCl 0.2% and distilled water. Plastic o-rings were replaced by Viton material whereas original plastic ribbons were replaced by silicone ribbons to avoid organic contamination. Samples were not filtered and were drawn as soon as possible after the rosette sampler was on the deck of the ship (before any other sampling). The 10 ml samples were collected in duplicate in precombusted (450° C, at least 6 hours) glass ampoules (Wheaton®). All ampoules were poisoned by addition of H₃PO₄ (final pH ~ 2) immediately after filling of ampoules, flame-sealed, and stored in the dark at 4°C for later analyses at the shore laboratory within 5 months. Other samples were analyzed on board by using the TOC 5000 unit equipped with a Licor detector. Quantification of this set of samples will be shown on another Table. Duplicate TOC were averaged for further calculations.

HTCO analysis

The Shimadzu instrument used in this study was the commercially available Model TOC-5000 Total Carbon Analyzer with quartz combustion column filled with 1.2% Pt on silica pillows with approximate diameter of 2 mm (Cauwet, 1994). Several aspects of our modified unit have been already described (Yoro et al., 1997; 1999 ; Dafner et al., 1999; 2000). A magnesium perchlorate water trap has been added to the system located before the halogen scrubber, and an in-line membrane filter and the non-dispersive infrared CO₂ detector. Prior to analysis, sub samples were sparged for 10 min with CO₂-free pure air at a gas flow rate of 40 ml min⁻¹ to remove inorganic carbon as CO₂. TOC contamination from the preservation reagent and from H₃PO₄ was below the detection limit. A hundred µl injections were repeated 3-4 times for each sample, the analytical precision of the procedure being within 3%, on average. Some variability in values from two different vials gives rise to a lower overall precision (10 %).

To bring the blank down, the catalyst was pre-treated by washing in 1% HCl and gently rinsed with DW, and dried in a furnace at a temperature of about 450°C for 10-15 min. Prior to analyses of standards and samples, the catalyst bed was 'conditioned' (during 1-3 days) by injecting 100 µl of acidified and sparged water from a high-quality water purifier, a Millipore Milli-Q Plus® System (hereafter DW), until the lowest stable integrated area was obtained. After two seawater sample injections the column was flushed by three injections of 100 µl of Milli-Q water. The catalyst was regenerated by using the TC catalyst function of the instrument once a week. Most of the time and after every two weeks of 25 daily samples injections, top of the catalyst (2 cm) was replaced was fresh material. The catalyst being completely renewed every three weeks.

Calibration of the instrument

Standardisation was carried out every day using potassium hydrogen phthalate (Kanto Chemical Company, Inc.) dissolved in DW prepared just before sample analyses. The instrument response factor, measured as the slope of the standard addition to DW ($r^2 > 0.999$ for 19 runs), remained relatively constant and reproducible over the time of analysis ($y = 6198x (\pm 202) + 713 (\pm 213)$)

The accuracy and the system blank of our instrument were determined by analysis of the Deep Atlantic Water (DAW) reference and low carbon water (LCW) from ampoules provided by D. Hansell. The average DOC concentration in the DAW reference and in the LCW

were $42 \pm 3 \mu\text{M C}$, $n = 63$ and $8.8 \pm 1.3 \mu\text{M C}$, $n=60$, respectively. Carbon level of LCW ampoules was similar and often higher than DW produced from our laboratory unit. TOC concentration in samples was calculated by averaging all replicate injections of samples, subtracting the average DW value as the total blank and dividing by the slope of the standardisation curve.