

Standard Operating Procedure for DOC analyses- Carlson Lab UCSB

DOC samples were analyzed via high temperature combustion using a Shimadzu TOC-V in shore based laboratory at the University of California, Santa Barbara. The operating conditions of the Shimadzu TOC-V were slightly modified from the manufacturer's model system. The condensation coil was removed and the headspace of an internal water trap was reduced to minimize the system's dead space. The combustion tube contained 0.5 cm Pt pillows placed on top of Pt alumina beads to improve peak shape and to reduce alteration of combustion matrix throughout the run. CO₂ free carrier gas was produced with a Whatman® gas generator (Carlson et al. 2004). Sample was drawn into 5 ml injection syringe and acidified with 2M HCL (1.5%) and sparged for 1.5 minutes with CO₂ free gas. Three to five replicate 100 μ l of sample were injected into combustion tube heated to 680° C. The resulting gas stream was passed through a several water and halide traps, the CO₂ in the carrier gas was analyzed with a non-dispersive infrared detector and the resulting peak area was integrated with Shimadzu chromatographic software. Injections continued until the at least three injection meet the specified range of a SD of 0.1 area counts, CV \leq 2% or best 3 of 5 injections.

Extensive conditioning of the combustion tube with repeated injections of low carbon water (LCW) and deep seawater was essential to minimize the machine blanks. After conditioning, the system blank was assessed with UV oxidized low carbon water. The system response was standardized daily with a four-point calibration curve of potassium hydrogen phthalate solution in LCW. All samples were systematically referenced against low carbon water and deep Sargasso Sea reference waters (2600 m)

and surface Sargasso Sea water every 6 – 8 analyses (Hansell and Carlson 1998). The standard deviation of the deep and surface references analyzed throughout a run generally have a coefficient of variation ranging between 1-3% over the 3-7 independent analyses (number of references depends on size of the run).

Daily reference waters were calibrated with DOC CRM provided by D. Hansell (University of Miami; Hansell 2005).

DOC calculation

$$\mu\text{MC} = (\text{average sample area} - \text{average machine blank area}) / (\text{slope of std curve})$$

Carlson, C.A., S.J. Giovannoni, D.A. Hansell, S.J. Goldberg, R. Parsons, and K. Vergin. 2004. Interactions between DOC, microbial processes, and community structure in the mesopelagic zone of the northwestern Sargasso Sea. *Limnology and Oceanography* 49: 1073-1083.

Hansell, D.A. and C.A. Carlson 1998. Deep ocean gradients in the concentration of dissolved organic carbon. *Nature*, 395: 263-266.

Hansell, D.A. 2005 Dissolved Organic Carbon Reference Material Program. EOS, 35:318-319.