

Standard Operating Procedure for TN analyses- Carlson Lab UCSB

TN samples were analyzed via high temperature combustion using a Shimadzu TOC-V with attached Shimadzu TNM1 unit at an 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. Carrier gas was produced with a Whatman® gas generator (Carlson et al. 2004) and ozone was generated by the TNM1 unit at 0.5L/min flow rate. Three to five replicate 100 μ l of sample were injected at 130mL/min flow rate into the combustion tube heated to 680° C, where the TN in the sample was converted to nitric oxide (NO). The resulting gas stream was passed through an electronic dehumidifier. The dried NO gas then reacted with ozone producing an excited chemiluminescence NO₂ species (Walsh 1989) and the fluorescence signal was detected with a Shimadzu TNMI chemiluminescence detector. The resulting peak area was integrated with Shimadzu chromatographic software. Injections continued until at least three injections 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 nitrogen water and deep seawater was essential to minimize the machine blanks. After conditioning, the system blank was assessed with UV oxidized low nitrogen water. The system response was standardized daily with a four-point calibration curve of potassium

nitrate solution in blank water. All samples were systematically referenced against low nitrogen water and deep Sargasso Sea reference waters (2600 m) and surface Sargasso Sea water every 6 – 8 analyses (Hansell and Carlson 1998). Daily reference waters were calibrated with deep CRM provided by D. Hansell (University of Miami; Hansell 2005).

TN calculation

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

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