

# Sampling guide for determination of dissolved organic carbon and total dissolved nitrogen in seawater

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Adapted from [Farmer and Hansell \(2007\)](#) by A.R. Margolin.

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For copies of this sampling guide:

[http://www.rsmas.miami.edu/groups/biogeochem/Data/DOC-TDN\\_Sampling\\_Guide.pdf](http://www.rsmas.miami.edu/groups/biogeochem/Data/DOC-TDN_Sampling_Guide.pdf)

For copies of sampling log:

[http://www.rsmas.miami.edu/groups/biogeochem/Data/DOC-TDN\\_Sampling\\_Log.pdf](http://www.rsmas.miami.edu/groups/biogeochem/Data/DOC-TDN_Sampling_Log.pdf)

[http://www.rsmas.miami.edu/groups/biogeochem/Data/DOC-TDN\\_Sampling\\_Log.docx](http://www.rsmas.miami.edu/groups/biogeochem/Data/DOC-TDN_Sampling_Log.docx)

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## i. Sampling summary

- Gloves should be worn during sampling ([Fig. 1](#)).
- It is recommended that anyone sampling from the rosette prior to collection of the samples also wear gloves.
- Every effort must be made not to touch the sample nipple.
- Grease should never be allowed to come in contact with the sample nipple.
- Tubing should be silicone ([Fig. 2](#)); under no circumstances should Tygon<sup>®</sup> tubing be used as it is a source of contamination.
- Label ([Fig. 3](#)) polycarbonate (PC) bottles ([Fig. 4](#)) with sample-specific information, i.e., cruise, station, cast and Niskin bottle numbers.

For DOC/TDN (same for TOC/TN except filter holder and filter are not required):

1. Using forceps ([Fig. 6](#)), place precombusted GF/F filter ([Fig. 8, 9](#)) in the inline filter holder ([Fig. 10, 11, 12](#)) underneath the O-ring ([Fig. 12, 13](#)) and cap filter holder ([Fig. 14](#)).
2. Connect filter holder to Niskin bottle ([Fig. 14](#)) and begin flowing sample through filter.
3. Tilt filter holder so air bubble is under vent cap ([Fig. 14](#)).
4. Carefully loosen vent cap to release air bubble, and quickly retighten the cap ([Fig. 14](#)).
5. Rinse pre-cleaned 60 mL PC bottle/cap ([Fig. 4](#)) adequately three times with filtrate.
6. Bottles should be filled to 75-90% (or ~50 mL) into the 60 mL PC bottle ([Fig. 4](#)).
7. The sample bottle should then be capped tightly and frozen upright.
8. Once frozen, samples should be placed in Ziploc<sup>®</sup> bags in an orderly fashion ([Fig. 16, 17](#)).

**ii. Photo summary**



**Figure 1.** Gloves for sampling. There should be multiple sizes and enough to share if needed.



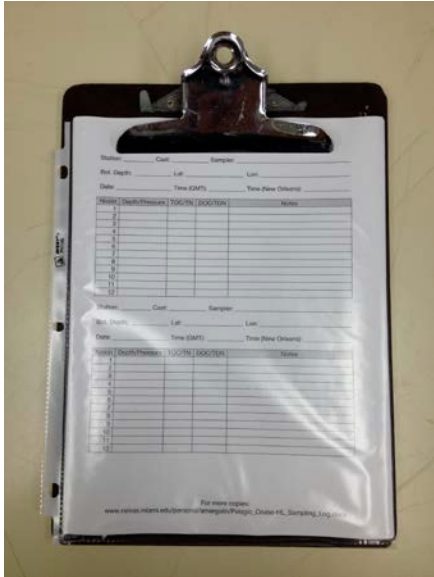
**Figure 2.** Inline filter holder with silicone tubing (two typically provided).



**Figure 3.** Writing utensils for labeling bottles (Fig. 4) and sampling logs (Fig. 5).



**Figure 4.** Pre-labeled PC sample bottles. Sampler will need to include station, cast and bottles numbers.



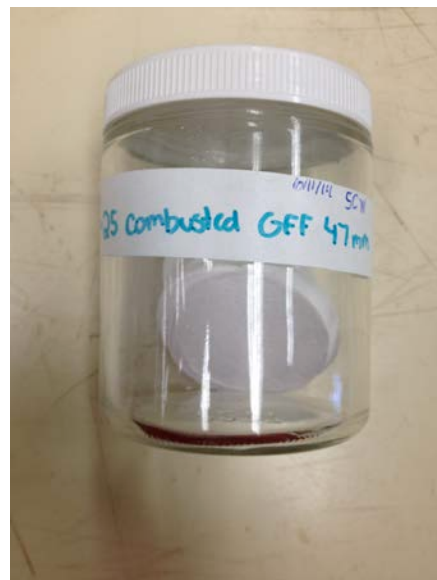
**Figure 5.** Sampling logs and clipboard. Plastic sleeve (if included) can be used for returning filled sampling logs in cooler with samples, or sampling logs can be scanned and emailed to W. Chen.



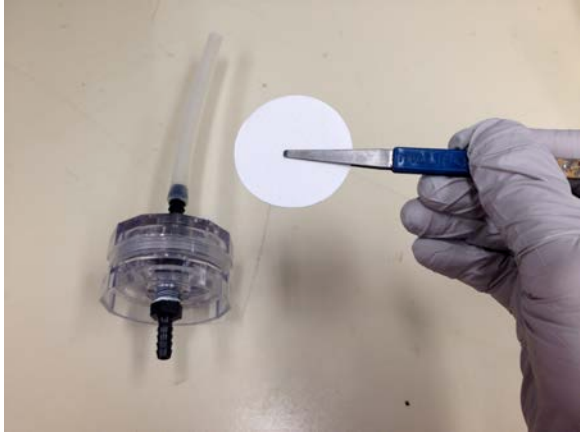
**Figure 6.** Forceps. Should be rinsed (Fig. 7) after removing used filter (i.e., after every station collection).



**Figure 7.** Clean rinse bottle for Milli-Q® water.



**Figure 8.** Pre-combusted GF/F filters. One is all that should be needed for each station.



**Figure 9.** A GF/F filter being handled with forceps before being placed in filter holder.



**Figure 10.** Two provided filter holders with silicone tubing.



**Figure 11.** Inline filter holder with O-ring removed.



**Figure 12.** Inline filter holder with O-ring removed and GF/F filter inserted.





**Figure 13.** Inline filter holder with O-ring placed on top of inserted GF/F filter.



**Figure 14.** Capped inline filter holder with GF/F filter inserted underneath O-ring. Connect silicone tubing to Niskin bottle, begin the flow of sample and tilt so air bubble is underneath vent cap. Carefully loosen vent cap to release air bubble, tighten, and then begin rinsing labeled PC bottle with filtrate three times before filling to ~50 mL mark. Bottles can be carried to Niskin bottle rosette using the provided sampling tray (Fig. 15).



**Figure 15.** Example of provided sampling tray. Can fit up to fifteen 60 mL PC bottles.



**Figure 16.** Ziploc® bags for storing frozen samples. Each bag can fit twenty-four 60 mL PC bottles.



**Figure 17.** Once all samples are collected and frozen, all samples and supplies can be packed into cooler for FedEx shipment (should be shipped for next-day delivery).

### **iii. Return address and shipping instructions**

Lillian Custals  
RSMAS/University of Miami  
4600 Rickenbacker Cswy.  
Miami, FL 33149  
USA

If there are questions or issues with shipping, contact Lillian Custals at 305-421-4049 (office) or [lcustals@rsmas.miami.edu](mailto:lcustals@rsmas.miami.edu).

## **1. Scope and field of application**

This procedure describes a method for the determination of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) in seawater, expressed as micromoles of carbon (nitrogen) per liter of seawater. The method is suitable for the assay of oceanic levels of dissolved organic carbon ( $< 400 \mu\text{mol L}^{-1}$ ) and total dissolved nitrogen ( $< 50 \mu\text{mol L}^{-1}$ ). The instrument discussed and procedure described are those specific to the instrument employed in the Hansell Laboratory at the University of Miami's Rosenstiel School of Marine and Atmospheric Science. Instruments produced by other manufacturers should be evaluated for suitability.

## **2. Definition**

The dissolved organic carbon content of seawater is defined as:

- *The concentration of carbon remaining in a seawater sample after all particulate carbon has been removed by filtration and all inorganic carbon has been removed by acidification and sparging.*

The total dissolved nitrogen content of seawater is defined as:

- *The concentration of nitrogen remaining in a seawater sample after all particulate nitrogen has been removed by filtration.*

## **3. Principle**

A filtered and acidified water sample is sparged with oxygen to remove inorganic carbon. The water is then injected onto a combustion column packed with platinum-coated alumina beads held at  $680^{\circ}\text{C}$ . Non-purgeable organic carbon compounds are combusted and converted to  $\text{CO}_2$ , which is detected by a non-dispersive infrared detector (NDIR). Non-purgeable dissolved nitrogen compounds are combusted and converted to  $\text{NO}$  which, when mixed with ozone, chemiluminesces for detection by a photomultiplier.

## **4. Apparatus**

Shimadzu TOC-L with ASI-L auto sampler and TNM-L total nitrogen detector.

## **5. Reagents**

Not included here. For more information, refer to [Farmer and Hansell, 2007](#).

## **6. Sampling**

Proper sampling techniques and handling are essential to good quality data. Care must be taken to minimize contamination of the sample. Sampling from the rosette should be done using clean silicone tubing. Gloves should be worn during sampling. It is recommended that anyone sampling from the rosette prior to collection of the samples (e.g., gases) also wear gloves. If that is not possible, every effort must be made not to touch the sample nipple (the path of the water stream, from Niskin to sample bottle, must be kept very clean). Grease (whether mechanical grease from ship operations or sealing grease, as employed for some gas sampling) should never be allowed to come in contact with the sample nipple.

### **6.1. Sample preparation**

Prior to sampling, 60 mL polycarbonate (PC) bottles are cleaned, first by rinsing with distilled water, followed by a 4-hour soak in 10% hydrochloric acid, and then copiously rinsed with distilled water, inverted onto a clean surface and allowed to air dry.

All tubing and the polycarbonate inline filter holder should be acid washed and rinsed with copious quantities of distilled water prior to use. Tubing should be silicone; under no circumstances should Tygon<sup>®</sup> tubing be used as it is a source of contamination.

GF/F filters should be combusted at 450°C for at least 4 hours prior to use and stored in a sealed glass container.

### **6.2. Sample collection**

Whether or not a sample is filtered prior to analysis depends on the goal of the measurement. If DOC and TDN are the variables of interest, then all samples must be filtered. However, the handling of water required for filtration can introduce contaminants, so in some cases filtration may be bypassed. In oligotrophic waters, e.g., where particulate organic carbon (POC)

concentrations may be a very small fraction of the total organic carbon, filtering may not be necessary. Since the particles are generally small and homogeneously distributed in a sample, the analysis of unfiltered water results in a good measure of TOC. Likewise, samples collected at depths > 250 m may be left unfiltered as water from these depths normally has low POC loads (< 1  $\mu\text{mol L}^{-1}$ ).

In high productivity areas, a substantial portion of the TOC may be present in particulate form, and many of those particles may be large and so not homogeneously and representatively assessed in the DOC analyzer. In those situations, samples collected between the surface and 250 m are filtered through a precombusted GF/F filter. For consistency when sampling in both oligotrophic and eutrophic environments as part of a study, prefiltering is recommended for all upper layer waters.

The GF/F filters are housed in a polycarbonate inline filter holder connected to the Niskin bottle sample nipple with silicone tubing, with collection of filtrate into a precleaned 60 mL PC bottle. PC sample bottles should be labeled with sample-specific information, such as the cruise designation, cast number, and Niskin bottle number. The filter holder, with filter in place, must be well flushed with sample prior to collection into the bottles. The sample bottles should be rinsed three times with sample prior to filling. Bottles should be filled to between 75 and 90%, or 45 to 55 mL into the 60 mL bottle. This volume provides room for expansion of the water on freezing. The sample bottles are then capped tightly and frozen upright.

## **7. Procedure**

Not included here. For more information, refer to [Farmer and Hansell, 2007](#).

## **8. Calculation and expression of results**

Not included here. For more information, refer to [Farmer and Hansell, 2007](#).

## **9. Quality assurance**

On a daily basis, DOC Consensus Reference Material (CRM; [Hansell, 2005](#); <http://www.rsmas.miami.edu/groups/biogeochem/CRM.html>) is analyzed to verify system

performance. If the value of the CRM does not fall within the expected range, samples are not analyzed until the expected performance has been established.

The Milli-Q<sup>®</sup> water blanks and reference seawater samples analyzed with the samples are used for quality assurance and quality control (QA/QC). By evaluating the performance of these reference waters, instrument drift and performance can be evaluated. If a problem is detected with either drift or performance, the samples are reanalyzed.

## References

- Farmer, C.T., Hansell, D.A. 2007. Determination of dissolved organic carbon and total dissolved nitrogen in sea water. In: A.G. Dickson, Sabine, C.L., Christian, J.R. (Eds.) *Guide to best practices for ocean CO<sub>2</sub> measurements*. PICES Special Publication 3, 191 pp. [http://cdiac.ornl.gov/ftp/oceans/Handbook\\_2007/sop07.pdf](http://cdiac.ornl.gov/ftp/oceans/Handbook_2007/sop07.pdf).
- Hansell, D.A. 2005. Dissolved Organic Carbon Reference Material Program. *EOS*, 86(35): 318. <http://onlinelibrary.wiley.com/doi/10.1029/2005EO350003/abstract>.