
Determination of dissolved organic carbon and total dissolved nitrogen in sea water

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 sea water, expressed as micromoles of carbon (nitrogen) per liter of sea water. The method is suitable for the assay of oceanic levels of dissolved organic carbon ($<400 \mu\text{mol}\cdot\text{L}^{-1}$) and total dissolved nitrogen ($<50 \mu\text{mol}\cdot\text{L}^{-1}$). The instrument discussed and procedures described are those specific to the instrument employed in the Hansell Laboratory at the University of Miami. 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°C . Non-purgeable organic carbon compounds are combusted and converted to CO_2 , which is detected by a non-dispersive infrared detector (NDIR). Non-purgeable dissolved nitrogen compounds are combusted and converted to NO , which when mixed with ozone chemiluminesces for detection by a photomultiplier.

4. Apparatus

Shimadzu TOC-V_{CSH} with ASI-V auto sampler and TNM-1 Total Nitrogen detector (or equivalent).

5. Reagents

5.1. Compressed gas

Ultra High Purity (UHP 99.995%) oxygen is used as the carrier gas for the Shimadzu TOC-V. High quality carrier gas is required to obtain low background levels in the detector. Oxygen is used to ensure complete combustion of all organic material.

5.2. Combustion Column Catalyst

The carrier gas passes through a column packed with 2 mm platinum-coated alumina beads (Shimadzu P/N 017-42801-01), held at 680°C.

5.3. Platinum Gauze

Pure platinum wire gauze (52 mesh woven from 0.1 mm diameter wire) is roughly formed into cubes (≈ 0.5 cm to a side) and several (3-5) are placed on top of the combustion column bed. The platinum gauze improves analytical reproducibility and retains injected salt.

5.4. Acidification of Sample

Trace-impurity analyzed concentrated hydrochloric acid is used to acidify samples prior to analysis. Approximately 0.1% by volume of the concentrated acid is added to each sample prior to analysis to lower the pH of the sample to $< \text{pH } 2$. At this pH and with sparging, all inorganic carbon species are converted to CO_2 and removed from the sample. Automated acidification by the TOC-V is not used as with time the blank using this acid solution increases. By manually acidifying the sample with acid freshly taken from a sealed bottle, the increase in blank has not been observed.

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 High Density Polyethylene (HDPE) 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® 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 glass airtight container.

6.2 Sample Collection

Whether or not a sample is filtered prior to analysis depends on the goal of the measurement. If DOC(N) is the variable of interest, then ideally 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, for example, where particulate organic carbon 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 total organic carbon (TOC). Likewise, samples collected at depths >250 meters may be left unfiltered as water from these depths normally have low particulate organic carbon loads (<1 μmole/liter).

In high productivity areas (nutrient rich zones), a substantial portion of the total carbon 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 60ml HDPE bottle. HDPE 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 3 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. Procedures

Water samples are collected from the rosette. Water taken from the surface to 250 m is filtered using precombusted (450°C) GF/F inline filters as they are being collected from the Niskin bottle. At depths >250 meters, the samples are collected without filtration. After collection, samples are frozen upright in 60 ml acid-cleaned HDPE bottles, and remain cold until analysis. Prior to analysis, samples are returned to room temperature and acidified to pH <2 with concentrated hydrochloric acid. Analysis is performed using a Shimadzu TOC-V_{CSH} Total Organic Carbon Analyzer with the TNM-1 Total Nitrogen detector.

Instrument conditions are as follows:

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| Combustion temperature | 680°C |
| Carrier gas | UHP Oxygen |
| Carrier flow rate | 150 ml/min |
| Ozone generation gas | Zero Air from Whatman TOC Gas Generator |
| Ozone flow rate | 500 ml/min |
| Sample sparge time | 2.0 minutes |
| Minimum number of injections | 3 |
| Maximum number of injections | 5 |

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|----------------------------|--------|
| Number of washes | 2 |
| Standard deviation maximum | 0.1000 |
| CV maximum | 2.00% |
| Injection volume | 100 µl |

Each detector functions independently with respect to the acceptance values above. If DOC meets the required specifications, but TDN does not, the instrument will continue making injections until either the criteria are met or the maximum number of injections has been reached. The same is true for the situation where TDN has met the criteria and the DOC has not.

The DOC system is calibrated using potassium hydrogen phthalate and the TDN system using potassium nitrate, both in Milli-Q water. System performance is verified daily using Consensus Reference Water (<http://www.rsmas.miami.edu/groups/biogeochem/CRM.html>). This reference water is deep Sargasso Sea water (DSR) that has been acidified and sealed in 10 ml ampoules, the concentrations of which (of DOC and TDN) has been determined by the consensus of up to six expert and independent laboratories. Low Carbon Water (LCW) that has gone through the same acidification, sealing process, and consensus verification program as the DSR and has an agreed upon carbon concentration of 1 to 2 µmoles C/L is also analyzed and used to determine the instrument blank. After verifying proper operation of the TOC/TN instrument, samples are placed on an auto sampler for analysis. The run starts with a QW (Q Water) blank and a reference seawater analysis. Then six samples are analyzed, followed by another QW blank and reference seawater. This sequence is repeated until all samples for that run are analyzed. The run ends with a QW blank, reference water, and a QW blank that had not been acidified. This last blank verifies that the hydrochloric acid used to acidify the samples is not contaminated. QW blanks and reference water samples are used to evaluate system performance during the analytical run. If a problem is detected with the blanks or reference waters, the samples are reanalyzed.

8. Calculation and expression of results

The Shimadzu TOC-V is calibrated for carbon using a 4 to 5 point analysis of potassium hydrogen phthalate in Milli-Q water. Since the instrument performs using units of parts per million (ppm), the concentration of the sample in µM (micromolar or micromoles per liter), and correction for the instrument blank, is calculated as:

$$[(\text{Sample (ppm)} - \text{LCW (ppm)}) \times 83.33333] + \text{LCW value } (\mu\text{M})$$

where Sample and LCW are the concentrations determined by the TOC-V, 83.33333 is a conversion factor converting ppm to µM and LCW is the carbon

concentration of the Low Carbon Water CRM. Subtracting the LCW (ppm) from the sample removes both instrument blank and carbon content of the LCW. The carbon content of the LCW is added again (final term in equation) to calculate the correct sample concentration.

For total dissolved nitrogen, the instrument is calibrated using a similar method to that used for calibrating total carbon. The standard is potassium nitrate in Milli-Q water. Again the instrument is calibrated in ppm and the following calculation is used to convert from ppm to μM :

$$\text{Sample (ppm)} \times 71.43$$

where sample is the concentration determined by the TOC-V and 71.43 is a conversion factor from ppm to μM . An instrument blank has not been detected for the nitrogen system. Dissolved Organic Nitrogen (DON) is calculated by subtracting inorganic nitrogen (NO_2 , NO_3 , etc) from the total dissolved nitrogen determined by the TOC-V.

9. Quality assurance

On a daily basis, Consensus Reference Water (CRM) 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 QW 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.

Citation:

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO₂ measurements. PICES Science Report No. 34.