

TOTAL ORGANIC CARBON (TOC) IN WATER SAMPLES

Introduction

A test for Total Organic Carbon, or one of its variants, is frequently used for monitoring water quality for drinking and treated waters, groundwaters, surface waters (eg lakes, rivers, stormwater), effluents, leachates and wastewaters.

Because of the various ways by which this test can be carried out, it is important to understand what is being measured so that the correct method can be used for your samples.

Definitions

Total Carbon (TC):

All of the carbon present in the sample. This includes both inorganic carbon (IC) and organic carbon (OC).

Total organic carbon (TOC):

All the carbon included in organic compounds in an aqueous sample.

Total inorganic carbon (TIC):

Carbon present in solution mainly as carbonate and bicarbonate, but also cyanide and thiocyanate.

Non-purgeable Organic Carbon (NPOC):

All the carbon present after the sample has been acidified and purged with purified air to remove inorganic carbon. Note that volatile organics such as volatile fatty acids (VFA), light hydrocarbons (eg petrol) and some solvents (eg acetone) will be lost during the purging. It is common but incorrect, for laboratories to measure NPOC, but report it as TOC.

Dissolved Organic Carbon (DOC) and Dissolved Non-purgeable Organic Carbon (DNPOC):

The organic carbon present after the sample has been filtered to remove particulate matter.

Analysis Methods

All common methods for measuring TOC rely on oxidising the carbon to carbon dioxide and then measuring this, often by thermal conductivity, but infrared spectrometry, conductivity, titration and conversion to methane followed by use of a flame ionisation detector are also used.

Methods for oxidising carbon

a) Combustion

The sample is homogenised, diluted if necessary, then injected into a heated reaction chamber containing a catalyst such as cobalt oxide. Water and carbon dioxide from both the organic and inorganic carbon present are released.

b) Persulphate Heat or UV oxidation

Organic carbon is released as carbon dioxide from a solution of persulphate into which the sample has been introduced. The reaction may be accelerated by either heat or UV light.

c) Titanium dioxide catalysed/UV light

Organic carbon is released as CO₂ after the sample is injected into a suspension of titanium dioxide which is circulated past a UV light. The CO₂ is measured by conductivity increase after absorption into ultrapure water in a conductivity cell.

Particulates

Most TOC analysers work with very small sample sizes, often only a few tens of microlitres, which are introduced into the instrument by a syringe needle. For this reason they will usually only cope with small particles, typically up to about 150 µm.

Effluent and waste samples must be well homogenised before analysis and this process may result in loss of volatile organics so this must be kept in mind when interpreting results.

Filtering for DOC/DNPOC

Samples MUST be filtered through inert filters, nylon is preferred.

We have found that it is very easy to contaminate samples during the filtering process, either from the filters or from the atmosphere.

A nylon HPLC grade filter is our recommendation for this. We also prefer that the filtering be done at our laboratory where a clean environment can be guaranteed.

Note that there may be changes in DOC samples with time after filtering. This is due to absorption or loss of CO₂ from/to the atmosphere and is also related to sample pH and temperature changes in the sample.

Containers for TOC

If low level TOC, etc, is to be measured than it is ESSENTIAL that very clean glass containers are used. Plastic is not suitable for low level analyses as plasticisers may leach out into the sample, but plastic containers may be used with effluents, etc, if the TOC is over 10 g.m⁻³.

We supply pre-cleaned (glassware dishwasher, oven baked) glass containers with Teflon lined lids for this purpose.

Hill Labs Capability

We can measure organic carbon in two different ways:

- Measure Total Carbon (TC), then acidify, purge off the CO₂ and measure this CO₂ (= Total Inorganic Carbon, TIC). Total Organic Carbon (TOC) is then given by TOC = TC – TIC
- Acidify and purge the sample before analysis. This gives NPOC (DNPOC on filtered samples).

See the table below for some suggestions on when to use each of these tests.

Our investigations have shown that, while the first method works well in many cases, if the TC is large (eg 51±5) and the TIC also large (eg 49±5) then TOC is being determined as the difference between two large numbers (51-49=2±7!). This has significant errors inherent in the determinations and we do not feel that results will be reliable if TC and TIC are both greater than about 15 and the TOC is less than 2. We thus prefer to report NPOC for these samples.

Which Organic Carbon Fraction to Analyse For?

The following are suggestions only as the required fraction will depend on different circumstances

	TOC	NPOC
Advantages:	Both volatile and non-volatile organics measured	Lower detection limit than TOC as inorganic carbon is purged from sample before analysis.
Disadvantages:	Detection limit not as low as NPOC because of possible high inorganic carbon.	Volatile organics are lost during purging process.
Use for:	Wastes and effluents where volatiles may be present and of interest eg tip leachates Drinking waters where Trihalomethanes (THM) are of interest	Samples open to the air so that variable purging will have occurred naturally eg surface waters (lakes, rivers, effluents, wastes), seawater Samples with high inorganic carbon
When to filter:	Groundwaters Wastes when only the soluble fraction is of interest	Groundwaters with high IC when low DL required Surface waters when only the soluble fraction is of interest