Total Organic Carbon (TOC) Total Nitrogen(TN) and Nutrients

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Chemical Nutrients

Natural Water

Inorganic

Nitrate
Nitrite
Phosphate
Ammonia
and many
more

Organic

Proteins
Carbohydrates
Humic acids

DNA
and more

Inorganic Nutrients	Organic Chemicals

Nutrient Analyzer

TOC and TN Analyzer

Seal AA500

Shimadzu TOC-L

Nutrient Analyzer - Seal AA500

Nutrient Analyzer

Autosampler Samples

Nitrite — Reagent 1
Reagent2
Reagent3

Phos — Reagent4
Reagent5

Ammo

Each Channel For One Nutrient

PUMP
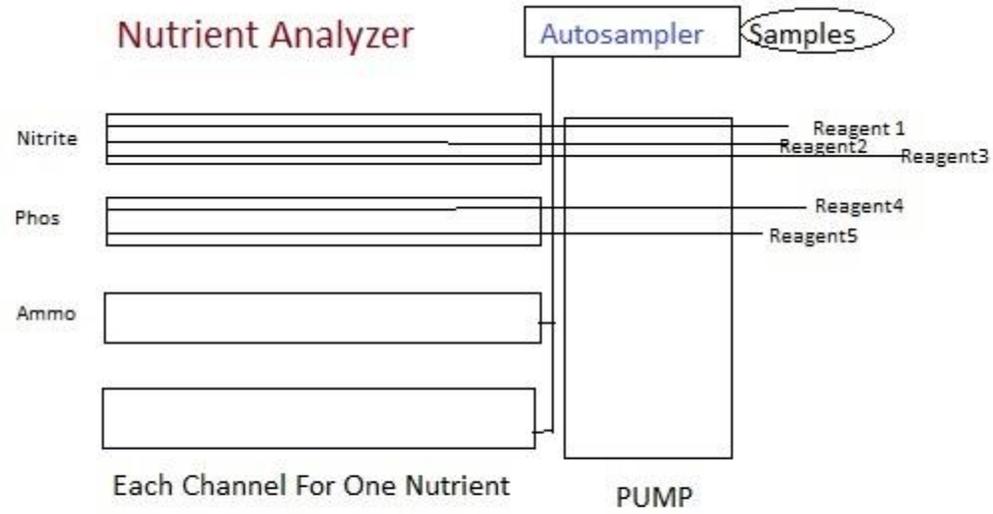
Total Carbon in Natural water

Researchers have been trying to find out how much dissolved organic matter (DOM) are in natural water for a long time. However, at present there is no real method to measure that. As a result, the best next thing is to measure the total organic carbon (TOC) in natural water.

Principles of Analysis

In a water sample, there are two types of carbon present: organic carbon and inorganic carbon.

Hydrogen, oxygen, and nitrogen attach to carbons to form organic compounds. We analyze for these carbons, and refer to these as Total Organic Carbon (TOC).

Inorganic carbon (IC) is basically the carbon from carbonate and bicarbonate in water. There are some dissolved Carbon dioxide in water as well.

Some Definitions we need to know

TC (Total Carbon), IC (Inorganic Carbon), Total Organic Carbon (TOC), Non-Purgeable Organic Carbon (NPOC).

TC = All the carbon in the solution. It is organic carbon plus inorganic carbon.

IC = carbon from carbonate and bicarbonate (and in dissolved CO2).

TOC = Carbon in the organic compounds. Basically, it is TC minus IC.

POC = These are organic materials that are volatile.

NPOC = For our purpose, this is the same as TOC.

Total Organic Carbon Instrument

TOC-L is the latest model from Shimadzu. This is a combustion system. This instrument does not require a wet oxidation chemical. It has a furnace that can reach 750 degrees C. The reactor with platinum catalyst is used to oxidize all carbons to carbon dioxide. The carbon dioxide will then be channeled into an Infrared detector for detection.

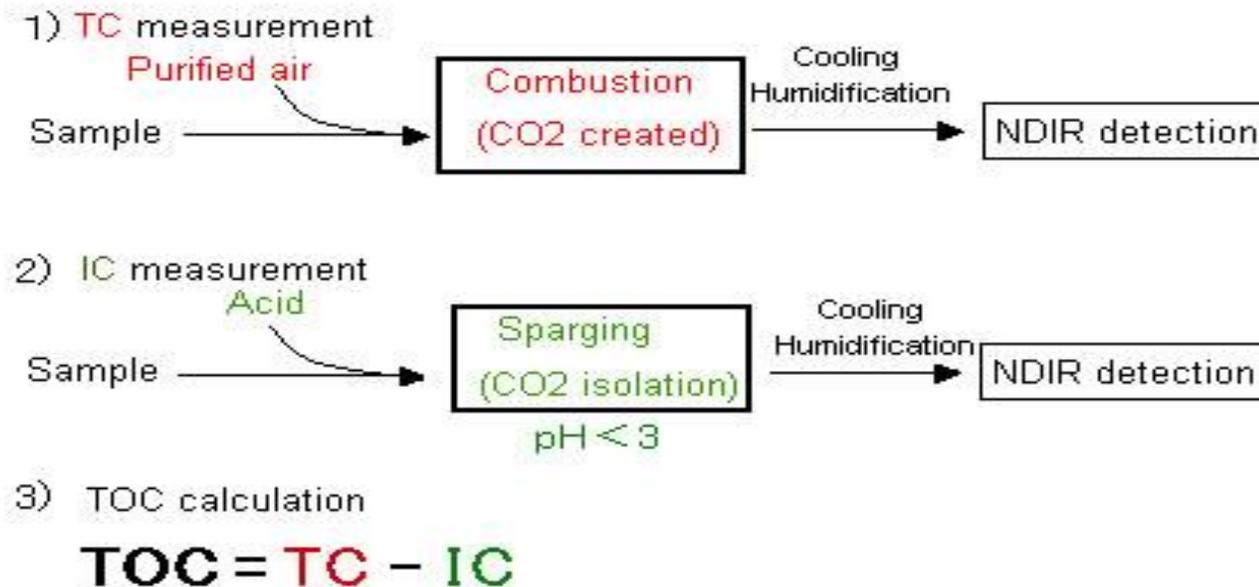# Two Methods For TOC analysis

1. TC and IC method

2. NPOC method

TC and IC Method of Analysis

In this method, we measure the total carbon (TC) and the inorganic carbon of a solution. Then calculate for TOC. The drawback here is if the sample has large IC and little TOC, then the accuracy may not be so good.
TOC = TC – IC

1) TC measurement

Purified air

Sample ⟶ Combustion (CO2 created) ⟶ Cooling Humidification ⟶ NDIR detection

2) IC measurement

Acid

Sample ⟶ Sparging (CO2 isolation) pH<3 ⟶ Cooling Humidification ⟶ NDIR detection

3) TOC calculation

$$TOC = TC - IC$$

NPOC Method

Another method for measuring TOC is to measure the NPOC in a solution. This method requires the addition of acid to the sample, to change all inorganic carbon to CO_2. Then the instrument purges the carbon dioxide out, before testing for carbon. The drawback for this method is if the sample has large amount of purgeable organic carbon (POC). For example; sample with volatile hydrocarbons.
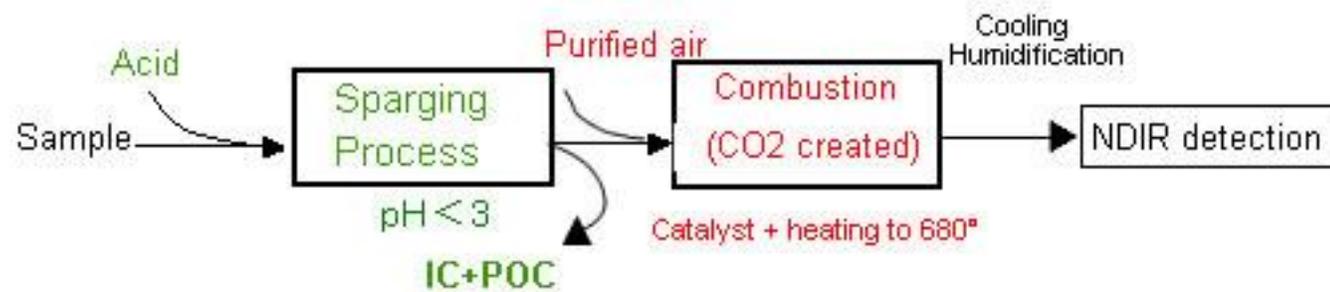
Schematic Diagram of NPOC Measurement

Preparation For Lab

All samples have to be filtered through a 0.45um filter. Two reasons for this; one is to protect the instrument. The other is to prevent particulates from causing inaccurate results. In addition, if you want to report the data as dissolved TOC, you must filter the sample.

The instrument we are using is from Shimadzu. It is the TOC-L system. Our system is configured to be used for both fresh and sea water. As a result, each sample has to be measured exactly 20 ml into a sample vial.

Standards for TOC, IC, NPOC.

For TOC and NPOC, standards are made from Potassium Hydrogen Phthalate. 2.125g/L = 1000 mg C/L

For IC, two inorganic materials are used; sodium hydrogen carbonate and sodium carbonate. 3.497 g sodium bicarb/L and 4.412 g sodium carbonate/L = 1000 mg C/L

Total Organic Nitrogen

In addition to measuring TOC, ETI has added a Total Nitrogen module to the system. As a result, the TOC-L also can be used to measure Total Nitrogen.
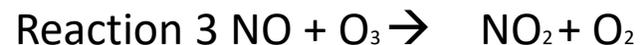
Total Nitrogen

1) Organic nitrogen: proteins, peptides, Nucleic acids, urea, and other natural and synthetic Nitrogen.
2) Inorganic Nitrogen: Nitrite, Nitrate, Ammonia

Principles of Measuring Total Nitrogen (TN)

The total nitrogen in a sample can be converted into nitrogen monoxide, by passing through a platinum catalyst reactor, at 720 degrees C. This is the method we use. The nitrogen monoxide formed can then be detected with a chemiluminescene gas analyzer, after Ozone reaction.

Reaction 1 $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Reaction 2 $2(NH_2)_2CO + 5O_2 \rightarrow 4NO + 4H_2O + CO_2$

Reaction 3 $NO + O_3 \rightarrow NO_2 + O_2$

Reaction 4 $NO + O_3 \rightarrow NO_2* + O_2$

Reaction 5 $NO_2* \rightarrow NO_2 + h\nu$

Total Nitrogen Instrument is one part of the TOC_L system. The TOC-L can be used to analyze for TN as well as TOC.

Standards for Total Nitrogen.

For TN, Potassium Nitrate is used.

Weight 7.219 g of Potassium Nitrate into a liter volumetric flask. Fill it with deionized water to the 1 L mark. This is equivalent to 1000 mg of total Nitrogen per liter (1000ppm).

Calculation:

Molecular weight of KNO_3 is 101.1032
Nitrogen is 14
So the ratio is 14/101.1032 = 0.13847
7.219 g of KNO_3 = 7219 mg KNO_3
7219 mg X 0.13847 = 999.63 = 1000 mg
In one liter, the final concentration is 1000mg / L

Note: This is 1000mg of Nitrogen in 1 liter. From this stock, we can prepare a few more standards.

Calculating The Concentration In Sample:

Usually 3 or 4 concentrations is enough, but you can use as many as you like. After we ran the standards, we can use Excel and graph the results onto an X-Y graph. The X axis can be concentration and the Y axis can be area under the peak or the peak height. Then we use this graph and the linear equation to calculate the concentration of total Nitrogen in our sample.

Let say we analyzed the sample and get 1000000 for peak area units. Using the linear equation of the standard graph, Y = 5792.8X + 16629. Rearrange to Concentration = X = (Y-16629)/5792. Y is the result peak height of the sample. In this case, X = 169.7 mg/L.

Alternately, you can use the graph of the standard curve.

Total Nitrogen Standard Curve

$y = 5792.8x + 16629$
$R^2 = 0.9996$