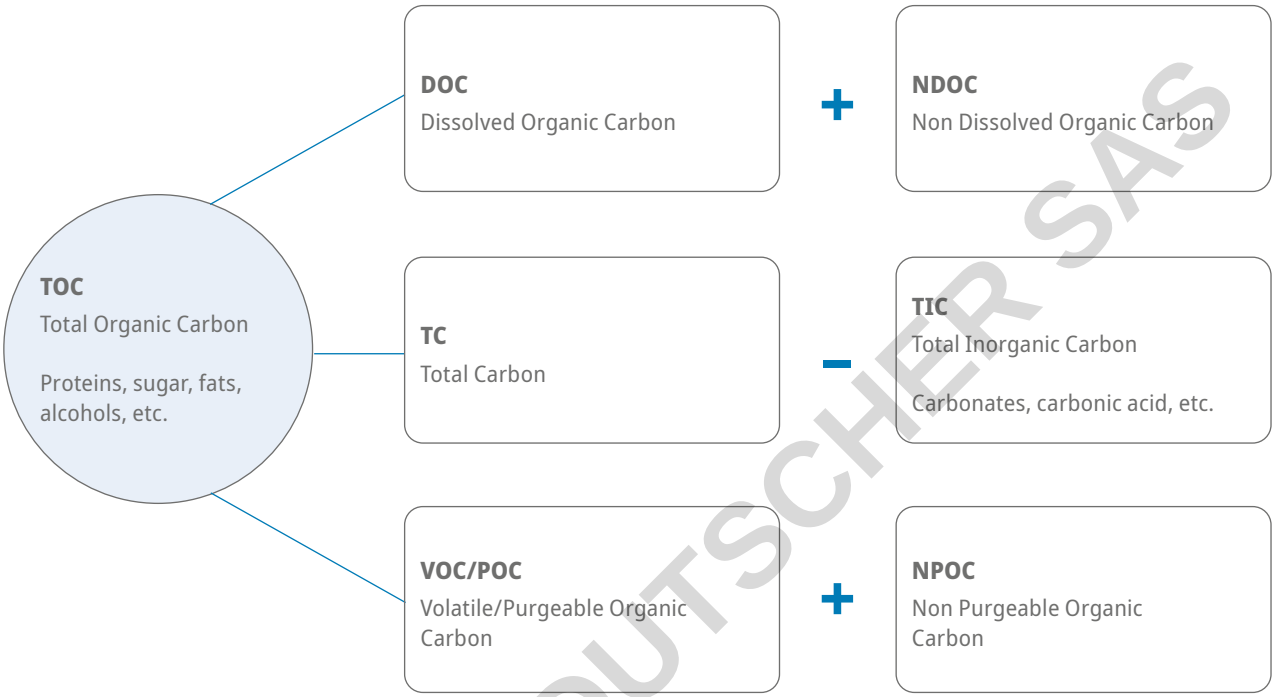
Practice report: toc analysis

# TOC – an insightful sum parameter




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## Introduction

In recent years, TOC has steadily gained in importance in wastewater analysis. In relationship to COD in particular, it provides specific information about the type and origin of organic loads in wastewater.

Advances have also been made in TOC analysis – no longer is a major investment required, either financially or in terms of equipment. The Hach® LCK Cuvette Test System enables the TOC content of water and wastewater to be measured reliably and cost effectively by both the purging and the difference method. Which of the two methods is the most suitable depends mainly on the composition of the analysis sample.

## What does TOC tell us?

TOC is, alongside or in association with COD and $BOD_5$, an important sum parameter for assessing the organic load of water. As all organic carbon compounds are determined and specified in terms of carbon mass, TOC is an exactly definable absolute quantity and is directly measurable (unit: mg/L C). TOC on its own sheds no light on the oxidisability of the measured carbon or the amount of oxygen needed for its biodegradation. However, the ratio COD:TOC provides important information about the presence of certain organic compounds (e.g. alcohols, proteins, etc.).
If this ratio changes, e.g. in the inflow of a sewage treatment plant, conclusions can be drawn immediately about the causes, and the possible effects on biological processes in the sewage treatment plant.




Cuvette test for TOC determination by the purging method

**Purging method**

The TOC is determined directly with just one measurement after the inorganic carbon (TIC) has been completely expelled from the sample (acidification + purging).

Especially suitable for samples with

- a TIC content that is much higher than their TOC content,
- a very low TIC content,
- a low TOC content.




Cuvette test for TOC determination by the difference method

**Difference method**

This involves two measurements, i.e. total carbon (TC) and total inorganic carbon (TIC). The TOC is then calculated as the difference between TC and TIC (TOC = TC – TIC).

Especially suitable for samples

- that contain volatile organic compounds (VOC),
- with a TOC content that is equal to or greater than their TIC content.

## Legal requirements

**Municipal wastewater:** According to the EU Council Directive (91/72/EEC, Annex I, table 1) concerning urban wastewater treatment, $BOD_5$ can be replaced as a monitoring parameter by TOC if a correlation can be established between the two parameters.

In some European countries, TOC has replaced COD as a monitoring parameter for official monitoring of effluents by authorities. In Germany, for example, TOC is officially used as a screening test in the context of COD monitoring of municipal wastewater. The COD of the wastewater is regarded as compliant if the TOC (in mg/L), multiplied by 4, does not exceed the COD limit value (see German Waste Water Ordinance – AbwV 1997, Article 6(3)).

**Industrial Waste Water:** Industrial Emission Directive (IED, 2010/75/EU) and the resulting new revised BREF's (best available treatment reference documents) recommend the use of TOC as preferred method because it does not rely on the use of compounds like mercury or potassium dichromate used for COD.

A basic problem associated with the switch from COD to TOC, however, is the often widely varying conversion factor. Depending on the composition of the wastewater, this factor can be between 2 and 6. Therefore parallel measurements of COD and TOC are needed to establish a plant specific COD:TOC ratio for wastewater treatment plants.

## TOC analysis: choice of method

All methods of measuring TOC are based on the thermal or wet chemical oxidation of organic carbon to carbon dioxide ($CO_2$). The carbon dioxide is detected and quantitatively determined. A distinction is made between two methods: the purging method and the difference method. The European standard EN 1484 refers to them both as equivalent reference methods. The choice of which method to use should be made on the basis of the composition of the sample. If, for example, the sample contains a large amount of volatile organic compounds (VOC), these will not be measured by the purging method (low-bias results).

The two methods may therefore provide widely different results for the same sample (due to the presence of VOC, or to unfavourable TC/TIC ratios). The method to be used for comparative measurements should therefore be agreed beforehand with, for example, supervisory bodies or external laboratories.

The comparability of TOC results usually depends not on the procedure but on the chosen measurement method (purging or difference method).

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## TOC cuvette test

If average numbers of samples have to be analysed, cuvette tests are the simplest and most cost-effective option. The chemicals and photometer are factory-calibrated and are therefore ready for immediate use.

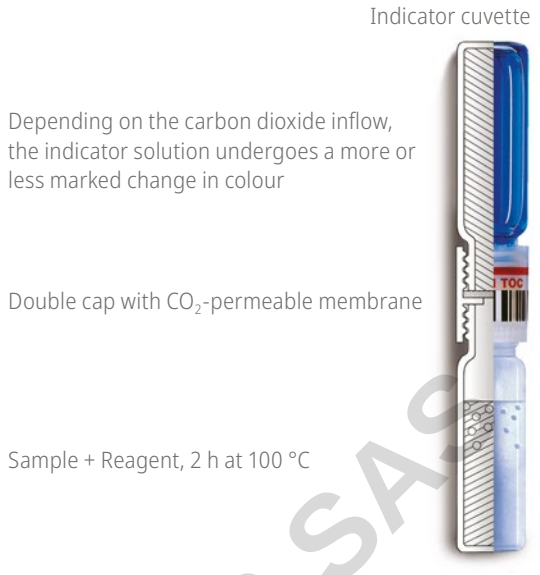
A wet chemical oxidative digestion is carried out, followed by photometric determination of the liberated carbon dioxide. The $CO_2$ passes from a digestion cuvette through a gas-permeable membrane and into an indicator cuvette. The resulting colour change in the indicator is evaluated photometrically.

A big advantage of this method is that even turbid, particle containing and coloured samples can be analysed without difficulty, as only the colour change in the indicator cuvette is measured.

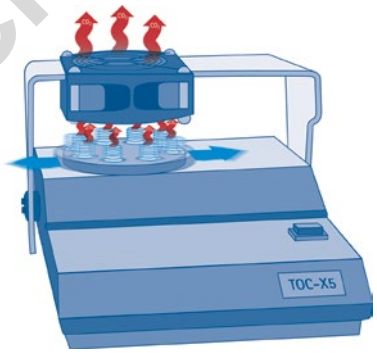
The purging method requires the inorganic carbon (TIC) to be removed from the sample before the digestion is carried out. The TOC-X5 shaker is used for this. The sample is simply pipetted into the digestion cuvette and the open cuvette is positioned in the shaker. The combination of shaker and fan drives all the TIC out of up to eight samples within just five minutes. The cap is then screwed onto the indicator cuvette and the TOC digestion in the thermostat can begin.

The shaker procedure saves time and is very easy and reliable from the point of view of handling.

- The correct amounts of all reagents are already present in the digestion cuvette.
- Analysis accessories do not need to be rinsed with TOC-free water.
- The three practical measuring ranges cover carbon concentrations from 3 - 3,000 mg/L, so that the homogenised sample can usually be analysed immediately, without any need for time-consuming prior dilution, which is also a potential source of error.




Functional principle of the LCK TOC Cuvette Test




Using the TOC-X5 shaker, the TIC is purged in just 5 minutes – from up to 8 samples simultaneously.

GHS Hazard Codes




Table 1: Overview of Hach TOC Cuvette Tests

| Method | Cuvette Test | GHS Code | Measuring Range | Sample preparation | Hach accessories |
|---|---|---|---|---|---|
| **Purging Method** | LCK385 | GHS07 GHS08 | 3 - 30 mg/L C | Homogenisation, purging, digestion | TOC-X5 shaker, thermostat, photometer |
| | LCK386 | | 30 - 300 mg/L C | | |
| | LCK387 | | 300 - 3,000 mg/L C | | |
| **Difference Method** | LCK380 | GHS03 GHS07 GHS08 | 2 - 65 mg/L C | Homogenisation, digestion | Thermostat, photometer |
| | LCK381 | | 60 - 735 mg/L C | | |

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# Analytics solutions for the determination of organic load



**Online UV Probe**
for continuous reagent-free determination of organic load via the spectral absorption coefficient (SAC)



**UV-VIS Spectrophotometer**
for evaluation of the TOC and all other LCK Cuvette Tests, plus for reagent-free determination of organic load via SAC



**Online TOC Analyser**
for continuous determination of TOC/TN/TP in challenging applications, e. g. containing fats, greases and oils as well as particulate loads



**Laboratory TOC Analyser**
for determination of TOC in drinking water, semiconductor and power applications



**Online TOC Analysers**
for continuous determination of TOC in condensate return, cooling and demineralised water, drinking water and effluent

**For more information please visit www.hach.com**

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