

Determination of TOC (0-1000ppm) and TN_b (0-100 ppm) in municipal wastewater according to EN 1484, USEPA 415.1 and 9060A

Background

- TOC is a valuable sum parameter in municipal waste water (WW) monitoring. It can be used as a more cost effective and non toxic surrogate for COD analysis for process control which also avoids production of toxic waste. TOC is also suitable for effluent control and is the required parameter for reporting in some countries.
- TN_b determination in the influent for process control and in the effluent for monitoring according to the EU-Directive can be conducted parallel to TOC measurement (according to NEN-ISO 20236 and ASTM D8083).
- Reliable, quick and direct detection of organic carbon content without interference of other parameters is possible.
- WWTPs that treat high amount of industrial discharges can monitor the influent for high organic load and react accordingly.
- Hach® QP1680 is a lab TOC analyser based on catalytic high temperature combustion technology. Its unique maintenance concept results in easy handling, that can be completed in a few quick steps.
- TOC monitoring in the effluent requires standardised determination in some regions.

Method

There are mainly two methods available to measure TOC.

NPOC

- Use this method if no volatile organics are present. When measuring with the QP1680 standard settings of the NPOC method, 650µl of 3N hydrochloric acid (HCl) are injected into the sample vial. Then oxygen is bubbled through the sample for 600s. This purges all IC from the sample. Afterwards the sample is injected into the oven and the TOC is measured.
- Ensure that the sample is acidified to pH<2. Alkalinity and pH of the sample may require additional sample preparation prior to the measurement.
- Ensure that all IC is sufficiently purged out of the sample by testing an aliquot of the sample spiked with IC.
- NPOC is equal to TOC, when VOC and POC are not present.

TOC = TC – IC Difference Method

- Use this method if volatile organics are present or if $\text{TOC} \geq \text{IC}$. Avoid this method if $\text{IC} > \text{TOC}$. For this method both, IC and TC are measured. The TOC is then calculated from the two individual measurements.
- When QP1680 measures IC with standard settings, 100µl HCl (3N) are added to 500µl of sample and the IC is purged out of the sample by bubbling oxygen through the sample. Ensure that all IC is purged out of the sample by testing an aliquot of the sample spiked with IC.
- The accuracy of the method is the sum of the accuracies of the two individual measurements. This means, that it is usually less accurate than the NPOC method. That is why the difference method should be avoided if $\text{IC} > \text{TOC}$.

The use of 3N HCl acid, 1N H₃PO₄ or 1.5N H₂SO₄ (more information in the Xpert manual available) is applicable for those two methods to determine TOC.

Determination of TOC and TN_b In Municipal Wastewater

TN_b

- TN_b analysis is based on the sum of inorganic and organic bound nitrogen which is measured under the high temperature combustion. The analysis can be carried out parallelly when measuring TC or NPOC.
- Generally speaking it is advisable to choose the calibration range so, that most measurements will be towards the middle of the range.
- Typical range TOC: 0-400 mg/L
- Typical range TN: 0-100 mg/L

Suggested TC/NPOC Calibration Range

0 – 1000 mg/L

Suggested IC Calibration Range

0 - 1000 mg/L

Suggested TN Calibration Range

0 – 250 mg/L

Analyser

QP1680 Lab TOC (High Temperature Combustion)

SETUP QP1680

- 1000µl syringe with a 0.8 mm ID needle
- Autosampler attached
- Sample glass vials (cleaned with ultrapure water and heated at 250°C for two hours)

NECESSARY LAB EQUIPMENT

- Water pre-treatment system for ultrapure water UPW (water purity min. 18.2 MΩ•cm, max. 1-2 ppb TOC), e.g. Millipore, ELGA, etc. Type 1 water (see Norm)
- Glassware: volumetric flasks with stoppers (appropriate size)
- Aluminium foil to cover sample vials (Part No. SM ...); alternatively, septum vials (Part No. SM...)



Calibration

Before calibrating the QP1680, make sure the blank value is below 50,000 AE and doesn't show a significant drift. To ensure that, run at least 10 blank measurements.

Calibration will be done with the calibration wizard.

TC and NPOC Calibration

The KHP (Potassium Hydrogen Phthalate) standard solutions at the right can be used for TC and NPOC calibration depending on the required calibration range.

The exact concentration of the standard solutions may differ slightly from the nominal value and can be found on the label of the container or bottle. For best results, please use that actual concentration of the respective standard for calibration. All standard solutions contain HCl and are therefore stable at room temperature for 1 month.

Product No. Concentration

LCW844	10 mg/L C standard solution (1 L)
LCW842	25 mg/L C standard solution (1 L)
LCW843	100 mg/L C standard solution (1 L)
LCW848	250 mg/L C standard solution (1 L)
LCW846	500 mg/L C standard solution (1 L)
2791505	1000 mg/L C standard solution 5 pc. 20mL glass vials

IC Calibration

For IC calibration Hach offers the standard solution at the right, which will be good for a few days after opening:

Use a mix of sodium hydrogen carbonate NaHCO₃ to make up IC stock solutions of higher concentration:

TIC stock standard solution 1000 mg/L C.

Add 7.04 g of sodium hydrogen carbonate of a 99.5 % mass fraction NaHCO₃ into ultra pure water. Add enough water to make the solution exactly 1 L. Mix well until all NaHCO₃ is dissolved in water.

Product No. Concentration

18149	240 mg/L IC Natriumcarbonat-standard solution, 0.02 N, 500 L
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TN Calibration

The following standard solutions can be used for TN calibration depending on the required calibration range.

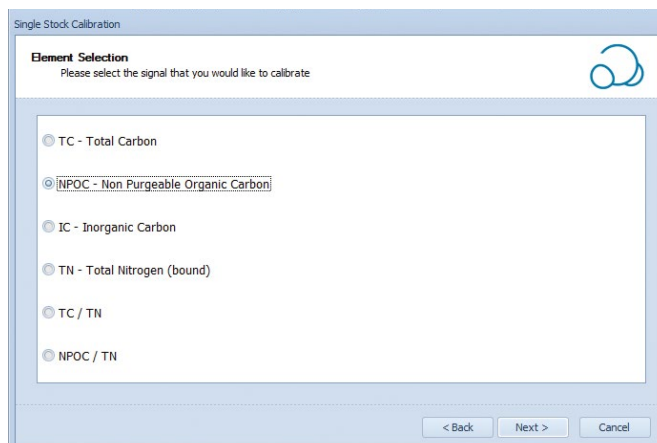
Product No. Concentration

204649	1 mg/L NO ₃ standard solution (500 mL)
30749	10 mg/L NO ₃ standard solution (500 mL) (this solution contains TOC)
194749	100 mg/L NO ₃ standard solution (500 mL)

Calibration Procedure

- Open the single stock calibration wizard.
- Choose the method to be calibrated e.g. NPOC for the calibration of NPOC. For the calibration of the difference method (TOC=TC-IC), both TC and IC must be calibrated. TC is best calibrated using a KHP standard solution. IC must be calibrated using a carbonate standard solution.
- Click "Next".
- Fill in the following parameters:
 - Concentration of stock solution (e.g. 500 mg/L)
 - Fill in the vial position of the stock solution
 - Select the method to be used →

NPOC/TN measuring flexible volume Veolia



Determination of TOC and TN_p In Municipal Wastewater

- Fill in the number of calibration points (recommended 10-points).
- Fill in how many replicates for every point should be run (recommended at least 3).
- Blank measurement is not necessary for calibration but it is necessary to condition the analyser beforehand.
- Click "Finish".

Single Stock Calibration

Calibration Line: 10/22/2021 NPOC 0-500 mg/L

Size: 10-Point Replicates: 3 Blank Position: 4

Name	Quantity	Origin (pos)	[C]
Blank	100	4	0.00
Std - [Concentration] mg/L	10	3	50.00
Std - [Concentration] mg/L	20	3	100.00
Std - [Concentration] mg/L	30	3	150.00
Std - [Concentration] mg/L	40	3	200.00
Std - [Concentration] mg/L	50	3	250.00
Std - [Concentration] mg/L	60	3	300.00
Std - [Concentration] mg/L	70	3	350.00
Std - [Concentration] mg/L	80	3	400.00
Std - [Concentration] mg/L	90	3	450.00
Std - [Concentration] mg/L	100	3	500.00

< Back Finish Cancel

- Now you will see an empty calibration list.

	Status	Sample ...	Outlier	Sig... ▲	Name	Concen...	Concent...	Mean	RSD	SD	Area	SampleType	Real ...	Quantity	Quanti...	Analyst	Densi...	Dilution	Calibration Line	Analysis Date
1	Not anal...	2			NPOC Std - 0.00 mg/L	0.00	mg/L					0.00 Calibration	0.00	100	µL	Lab manager	1	1		
2	Not anal...	2			NPOC Std - 0.00 mg/L	0.00	mg/L					0.00 Calibration	0.00	100	µL	Lab manager	1	1		
3	Not anal...	2			NPOC Std - 0.00 mg/L	0.00	mg/L					0.00 Calibration	0.00	100	µL	Lab manager	1	1		
4	Not anal...	1			NPOC Std - 50.00 mg/L	0.00	mg/L					0.00 Calibration	50.00	100	µL	Lab manager	1	1		
5	Not anal...	1			NPOC Std - 50.00 mg/L	0.00	mg/L					0.00 Calibration	50.00	100	µL	Lab manager	1	1		
6	Not anal...	1			NPOC Std - 50.00 mg/L	0.00	mg/L					0.00 Calibration	50.00	100	µL	Lab manager	1	1		
7	Not anal...	1			NPOC Std - 100.00 mg/L	0.00	mg/L					0.00 Calibration	100.00	100	µL	Lab manager	1	1		
8	Not anal...	1			NPOC Std - 100.00 mg/L	0.00	mg/L					0.00 Calibration	100.00	100	µL	Lab manager	1	1		
9	Not anal...	1			NPOC Std - 100.00 mg/L	0.00	mg/L					0.00 Calibration	100.00	100	µL	Lab manager	1	1		
10	Not anal...	1			NPOC Std - 150.00 mg/L	0.00	mg/L					0.00 Calibration	150.00	100	µL	Lab manager	1	1		
11	Not anal...	1			NPOC Std - 150.00 mg/L	0.00	mg/L					0.00 Calibration	150.00	100	µL	Lab manager	1	1		
12	Not anal...	1			NPOC Std - 150.00 mg/L	0.00	mg/L					0.00 Calibration	150.00	100	µL	Lab manager	1	1		
13	Not anal...	1			NPOC Std - 200.00 mg/L	0.00	mg/L					0.00 Calibration	200.00	100	µL	Lab manager	1	1		
14	Not anal...	1			NPOC Std - 200.00 mg/L	0.00	mg/L					0.00 Calibration	200.00	100	µL	Lab manager	1	1		
15	Not anal...	1			NPOC Std - 200.00 mg/L	0.00	mg/L					0.00 Calibration	200.00	100	µL	Lab manager	1	1		
16	Not anal...	1			NPOC Std - 250.00 mg/L	0.00	mg/L					0.00 Calibration	250.00	100	µL	Lab manager	1	1		
17	Not anal...	1			NPOC Std - 250.00 mg/L	0.00	mg/L					0.00 Calibration	250.00	100	µL	Lab manager	1	1		
18	Not anal...	1			NPOC Std - 250.00 mg/L	0.00	mg/L					0.00 Calibration	250.00	100	µL	Lab manager	1	1		
19	Not anal...	1			NPOC Std - 300.00 mg/L	0.00	mg/L					0.00 Calibration	300.00	100	µL	Lab manager	1	1		
20	Not anal...	1			NPOC Std - 300.00 mg/L	0.00	mg/L					0.00 Calibration	300.00	100	µL	Lab manager	1	1		
21	Not anal...	1			NPOC Std - 300.00 mg/L	0.00	mg/L					0.00 Calibration	300.00	100	µL	Lab manager	1	1		
22	Not anal...	1			NPOC Std - 350.00 mg/L	0.00	mg/L					0.00 Calibration	350.00	100	µL	Lab manager	1	1		
23	Not anal...	1			NPOC Std - 350.00 mg/L	0.00	mg/L					0.00 Calibration	350.00	100	µL	Lab manager	1	1		
24	Not anal...	1			NPOC Std - 350.00 mg/L	0.00	mg/L					0.00 Calibration	350.00	100	µL	Lab manager	1	1		
25	Not anal...	1			NPOC Std - 400.00 mg/L	0.00	mg/L					0.00 Calibration	400.00	100	µL	Lab manager	1	1		
26	Not anal...	1			NPOC Std - 400.00 mg/L	0.00	mg/L					0.00 Calibration	400.00	100	µL	Lab manager	1	1		
27	Not anal...	1			NPOC Std - 400.00 mg/L	0.00	mg/L					0.00 Calibration	400.00	100	µL	Lab manager	1	1		
28	Not anal...	1			NPOC Std - 450.00 mg/L	0.00	mg/L					0.00 Calibration	450.00	100	µL	Lab manager	1	1		
29	Not anal...	1			NPOC Std - 450.00 mg/L	0.00	mg/L					0.00 Calibration	450.00	100	µL	Lab manager	1	1		
30	Not anal...	1			NPOC Std - 450.00 mg/L	0.00	mg/L					0.00 Calibration	450.00	100	µL	Lab manager	1	1		
31	Not anal...	1			NPOC Std - 500.00 mg/L	0.00	mg/L					0.00 Calibration	500.00	100	µL	Lab manager	1	1		
32	Not anal...	1			NPOC Std - 500.00 mg/L	0.00	mg/L					0.00 Calibration	500.00	100	µL	Lab manager	1	1		
33	Not anal...	1			NPOC Std - 500.00 mg/L	0.00	mg/L					0.00 Calibration	500.00	100	µL	Lab manager	1	1		

Recommendations

- It is best practice to add a stir bar to the sample vial to ensure good homogenisation during the measurement. This is particularly important when particles are present in the sample.
- Particles larger than 800µm may clog the needle and should be removed before analysis.
- Minimise the contamination of the system by running an appropriate number of blank water samples prior to calibrations and samples. The blank value should be lower than 50,000 AU and stable.
- It is necessary to analyse quality control standards on a regular basis (at least daily) to ensure the validity of the calibration. The software allows the analyst to automatically bracket the continuing quality control standards within the sample run file.

Maintenance

- Refresh the UPW in the UPW bottle and the humidifier daily.
- Every week refresh the acid from the acid bottle (Use 3N HCl).
- After refreshing the reagents always run the system method "Fill tubing sampler with liquids".

Fill tubing sampler with liquids ▼

- On a daily basis: before analysing samples, check the injection port for leakages by putting a droplet of water onto the furnace port. If you see bubbles, clean the injection port and test again. If there is still gas coming out of the furnace port, replace the furnace port. Chapter 17.14 in the manual explains the maintenance of the Injection port.
- Carefully clean the sample needle if salt or other solids build up on the outside.
- Clean the IC and waste port if salt or other solids build up on them.
- The method of standard addition (spiking) and/or dilution of the sample can be used to understand matrix effects.
- If the quality control measurement reveals too low recovery, it is necessary to recalibrate the instrument. Eventually it will be necessary to replace the furnace and/or catalyst completely.

Compliance

TOC/NPOC:

ASTM D7573

EN 1484

EPA 415.1

EPA 9060A

ISO 8245

SM 5310B

NEN-ISO 20236

TN_b:

ASTM D8083

EN 12260

ISO11905-2

NEN-ISO 20236