

# Total Organic Carbon in water matrices using the HiPerTOC analyzer

## Key Words

- Total Organic Carbon
- TOC
- NPOC
- Surface Water
- Waste Water
- Tap Water

## Introduction

Total Organic Carbon (TOC) analysis is a fast screening parameter for any organic carbon present in water. Nowadays TOC value is a crucial parameter for drinking water and wastewater treatment plants. For drinking water TOC gives an indication of the presence of organic compounds. These compounds are potentially dangerous in the cleaning process. They may react with the disinfectants to form toxic and even carcinogenic compounds. High TOC concentrations in wastewater may cause eutrophication, which lead to rapid oxygen depletion. The lack of oxygen then causes massive mortality among fauna and fish.

With the HiPerTOC analyzer water or environmental laboratories can use 4 different destruction techniques to cover all water matrices. They can analyze clean matrix samples like ultra-pure water up to heavy matrix samples like seawater.

This application report describes the use of two destruction techniques: High temperature destruction and UV/persulfate destruction. These two destruction techniques are suitable to measure drinking water, surface water and percolate water (mixture of soil and acid tear eluates). Adding a known amount of TOC to the samples tests the matrix dependence of the TOC analysis.

## Referenced Documents

The HiPerTOC analyzer complies with the following standard methods:

- |              |  |
|--------------|--|
| EN 1484:     | Water analysis: Guidelines for the determination of Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC)  |
| ASTM D 4839: | Total Carbon and Organic Carbon in Water by UV-persulfate Oxidation, and/or Infrared Detection TC, IC, TOC in water, waste water and sea water                           |
| ASTM D 4779  | Total, Organic and Inorganic Carbon in High Purity Water by UV persulfate Oxidation and/or Infrared Detection TC, IC, TOC in production water, high purity process water |

## Principle of operation

The TOC principle used for this application note is known as the NPOC method (non purgeable organic carbon). This means that the inorganic carbon and purgeable carbon compounds are removed prior analysis and not measured. The auto sampler of the HiPerTOC can do this automatically. The auto sampler adds acid to the sample vial. All inorganic carbon is unstable at low pH and reacts to CO<sub>2</sub>. The auto sampler then bubbles gas through the sample to homogenize and sparge off all the purgeable compounds, i.e. CO<sub>2</sub> and some volatile carbon compounds. The sparged sample, containing only organic carbon, is ready to be analyzed for TOC.

The built-in XYZ auto sampler draws some of the sample from the vial and, depending on the preferred destruction method, it injects the sample into the high temperature reactor or the uniquely designed UV-reactor. The user chooses the destruction technique per sample in the ThEuS software. The analyzer can switch from high temperature oxidation to UV-persulfate oxidation and back without user intervention.

For the application of the high temperature oxidation no catalyst is present and the temperature is 1,000 °C. The carrier gas leads the CO<sub>2</sub> to the dual NDIR detector via a condition step. The absorbed Infra Red radiation is relative to the amount of CO<sub>2</sub>, which relates to the total organic carbon in the sample.

For the application of the UV-reactor the UV-light supported by the persulfate reagent destroys the samples. The special design of the reactor optimizes the contact surface of the UV-lamp with the sample. This gives a very high destructive power of the UV-persulfate method ensuring full and fast oxidation. The carrier gas again leads the CO<sub>2</sub> through a conditioning step to the detectors.

The dual NDIR detectors measure the CO<sub>2</sub> simultaneously within two analytical ranges. One detector is 10 times more sensitive than the other. So, high and low TOC values are reported in one run, without dilution and re-measuring the out-of-range samples.

ThEuS software supports several multiple point calibration lines per sample queue. Working ranges used are standard or customers defined. Generated data and peaks can be recalculated afterwards, or during analysis.

## Samples preparation

The five types of samples are tap water, two surface waters from the rivers Schie (Delft, The Netherlands) and Seine (Paris, France), a waste water and a percolate water (mixture of soil and acid tar eluates). Adding known amounts of TOC to the sample can test for matrix dependency of the analyses. Putting 2 ml of 500 mg/L anhydrous potassium hydroxyl phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) in a 100 ml volumetric flask and filling to the mark with the sample spikes the specific sample with 10 mg/L TOC. Analogue to this, 5 ml of 1,000 mg/L  $\text{KHC}_8\text{H}_4\text{O}_4$  spikes the specific sample with 50 mg/L TOC. Table 1 lists an overview of the samples and their additions.

SAMPLE	ORIGIN	ADDITION (mg TOC/L)
1	Tap water	0
2	Tap water	10
3	Tap water	50
4	Schie	0
5	Schie	10
6	Schie	50
7	Seine	0
8	Seine	10
9	Seine	50
10	Waste water	0
11	Waste water	10
12	Waste water	50
13	Percolate	0
14	Percolate	10
15	Percolate	50

Table 1: Sample preparation details

## System settings

Temperature:	1,000°C for HT, 85 °C for UV
Carrier gas:	Oxygen, 250 mL/min
Sample volume:	1000 µL
Injection speed:	25 µL/s
Sampler:	Built-in XYZ-sampler

## Calibration

The calibration stock solution contains 21.25g anhydrous potassium hydroxyl phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) in 1 liter of ultra pure water, giving 10 g organic carbon per liter (10,000 mg/L). Diluting the stock solution 10 and 20 times gives the standards of 1,000 and 500 mg/L TOC to use for the addition, as described under Sample Preparation. For the calibration line eight calibration standards are prepared by dilution giving 2.5, 5, 10, 25, 50 and 100 mg carbon per liter for calibrating the high temperature and UV-persulfate method.

## Results

Table 2 lists the integrated signals of the high sensitive detector for the standard measured with the high temperature and UV-persulfate methods. Graph 1 and graph 2 plot the relations between the integrated signals and the concentrations of the standards. Table 3 shows the TOC concentrations of the samples by high temperature and UV-persulfate destruction. Table 3 also lists the reproducibility of the samples at 5 replicates, the recovery of the spikes and the comparison of the TOC concentrations by both destructions.

### Equation 1 calculates the recovery:

$$\text{Recovery} = \frac{(C_5 - C_0)}{S} \times 100\% \quad (1)$$

$C_0$  = Concentration of sample (mg / L)

$C_5$  = Concentration of spiked sample (mg / L)

$S$  = Added concentration to spiked sample (mg / L)

### Equation 2 calculates the comparison:

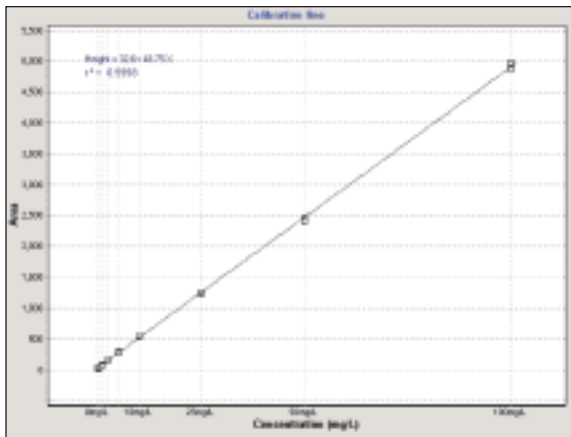
$$\text{Comparison} = \frac{C_{\text{HT}}}{C_{\text{UV}}} \times 100\% \quad (2)$$

$C_{\text{HT}}$  = Concentration on high temperature (µg / L)

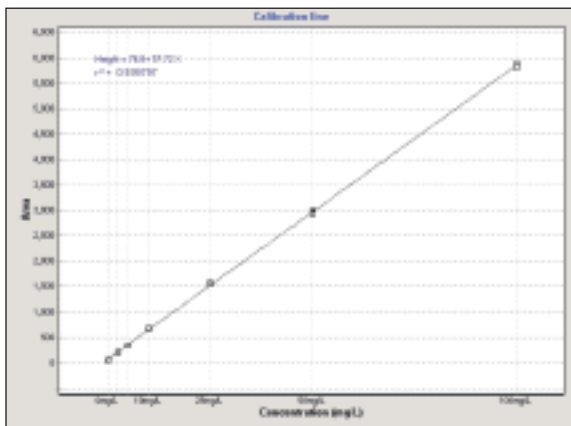
$C_{\text{UV}}$  = Concentration on UV – persulfate (µg / L)

STANDARD (mg/L)	AREA (mV*s)	
	HIGH TEMPERATURE	UV-PERSULFATE
0	37.9	56.8
2.5	164.6	209.6
5.0	280.2	343.3
10.0	539.8	675.9
25.0	1252.9	1561.8
50.0	2408.3	2964.4
100.0	4923.1	5836.7

Table 2. Calibration results



Graph 1: Calibration line for high temperature



Graph 2: Calibration line for UV-persulfate

SAMPLE	HIGH TEMPERATURE			UV-PERSULFATE			RELATIVE DEVIATION HT/UV(%)
	MEAN (mg C/L)	RSD(%)	RECOVERY(%)	MEAN (mg C/L)	RSD(%)	RECOVERY(%)	
Tap water	2.5	3.0		2.7	3.1		93
Tap water + addition 10	12.8	1.6	103	13.7	0.3	110	93
Tap water + addition 50	54.7	1.3	104	52.9	1.3	100	103
Schie	13.9	2.9		15.2	0.8		91
Schie + addition 10	24.8	2.9	105	24.7	0.5	95	99
Schie + addition 50	66.1	1.0	104	62.7	0.6	95	105
Seine	4.6	4.1		3.1	3.3		148
Seine + addition 10	14.8	2.9	102	13.7	0.8	106	108
Seine + addition 50	57.7	1.6	106	51.1	0.7	96	113
Waste water	43.1	2.2		37.5	0.8		115
Waste water + addition 10	51.9	3.9	88	45.6	0.3	81	114
Waste water + addition 50	92	2.7	98	81.7	0.2	88	113
Percolate	3.6	4.1		5.2	1.9		69
Percolate + addition 10	14.3	2.2	107	15.9	1.0	107	90
Percolate + addition 50	54.4	4.1	102	57.8	1.4	105	94

Table 3. Results of the sample with RSD (n=5)

## Discussions

The TOC analysis with high temperature and UV-persulfate oxidation show good linearity of 0.9998 for both techniques. The recovery of the spikes is in general around 100% within a 10% margin, except for the waste water samples. It is likely that this sample matrix is not stable, i.e. bacteria from the waste water treatment plant digest the organic carbon. This effect is even clearer for the waste water sample oxidized with UV-persulfate. Bacteria had more time to digest the organic carbon, since the UV-persulfate method has been run after the high temperature method. TOC analysis of the percolate samples with UV-persulfate oxidation show higher concentrations compared to the high temperature oxidation. It seems that the UV-persulfate method has more destructive power for this matrix.

## Conclusions

The HiPerTOC shows excellent linearity for lower TOC concentration (0-100ppm) on both destruction methods. Oxidation by high temperature or UV-persulfate gives comparable results for tap water and surface waters. The high temperature method gives higher TOC concentration in waste water samples than the UV-persulfate method. UV-persulfate method gives higher TOC concentration in percolate samples than the high temperature method. More investigation is necessary for these matrices.

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