Flakes, fibers and partic

TOC-V_{CPH} with the ASI-V autosampler and PC

The chemical oxygen demand (COD) parameter is increasingly being replaced by the total organic carbon (TOC) as a suitable parameter in wastewater analysis. This results in reduction of environmentally hazardous chemicals, and in the long term in cost reduction due to the high level of automation and low operating costs of a modern TOC measuring station. Depending on their origin, different types of wastewater samples can contain considerable amounts of insoluble particles. These sample components are clearly visible. In particular heavy particles such as sand will often sediment rapidly.

Suspended particles such as fibers or flakes are less susceptible to sedimentation. They will, however, result in sample matrix inhomogeneity. A variation of TOC determination is the determination of dissolved organic carbon (DOC). During DOC, the wastewater sample is filtered through a 0.45 µm pore size membrane filter, and the filtrate is subsequently measured. In contrast with DOC, TOC determinations detect the total amount of organic carbon in a sample, including the insoluble components. According to DIN EN 1484, the suitability of a TOC measuring instrument for the analysis of wastewater samples that contain particles must be tested. This is carried out using the so-called cellulose test (Attachment C of DIN EN 1484).

Cellulose test according to DIN EN 1484

The cellulose test is based on an aqueous cellulose suspension with a carbon content of 100 mgC/L. This corresponds to 225 mg of cellulose. The particle size is within a 20 µm up to 100 µm range. Homogenization may only be carried out using stirring. Alternative procedures such as ultrasound can break up and reduce the size of the particles and thereby distort the results.

Larger particles especially, have a tendency toward rapid sedimentation. The stirring intensity is therefore important. Very slow stirring results in strong particle sedimentation, while extremely high stirring speeds will lead to inhomogeneous particle distribution due to the centrifugal force. The DIN 38402 part 30 norm applying to sample homogenization can be helpful here. According to this standard, a liquid should be stirred in such a way that the vortex is 10 % of the filling height.

Cellulose standard (100 mgC/L)	Injections (n)	TC (mgC/L))	RSD (%)
Experiment 1	3	103	4.62
Experiment 2	3	99	4.07

Table 1: DIN-Cellulose test – results

For three consecutive injections, the average value must be in the range of 90 mg/L to 110 mg/L (recovery rate 90 - 100 %). The relative standard deviation (RSD) should not be higher than 10 %.

This test was carried out on a TOC-V system (TOC-V_{CPH} including autosampler ASI-V with integrated stirring option). The two experiments below were carried out consecutively and the results are shown in Table 1.

The data are within the specification range according to DIN. However, closer inspection of the standard material raises a suspicion that the data include outliers. Based on this assumption, additional experiments on a larger number of consecutive injections were carried out via the offline-port. Table 2 shows two experiments with the cellulose standard, each based this time on 10 injections. In addition, all individual results are shown in Figure 1.

These results clearly demonstrate the suitability of the Shimadzu TOC-V series analyzers for samples containing suspended particles and with respect to the testing conditions according to DIN EN 1484 and beyond. However, real wastewater samples can be homogenized very effectively, since additional procedures are available in addition to stirring.

Wastewater

Reproducible TOC measurements require a homogeneous sample matrix. For real wastewater samples this is often not feasible and an effective sample pretreatment procedure is therefore required. The 'Ultraturrax' has proven to be a reliable tool. Solid sample components, including even small sand particles are effectively homogenized. This results in suspensions that will sediment only moderately. TOC as well as NPOC measurements show clearly improved results compared to

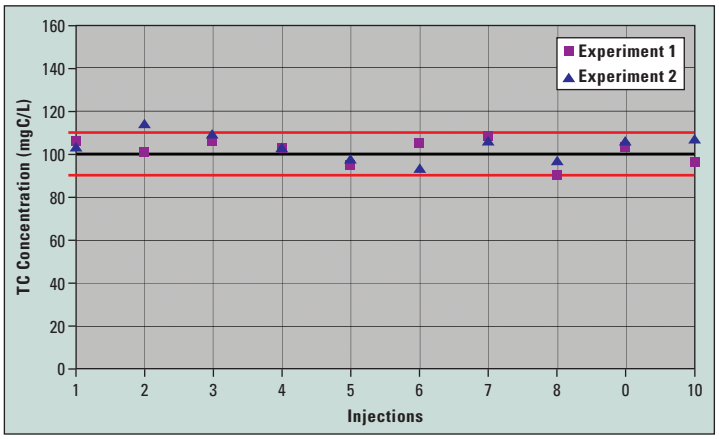

Figure 1

les – TOC in wastewater

Cellulose standard (100 mgC/L)	Injections (n)	TC (mgC/L)	RSD (%)
Experiment 1	10	102	5.74
Experiment 2	10	104	5.95

Table 2: Cellulose test – 10 injections

Sample	Injections (n)	NPOC (mgC/L)	RSD (%)
*Wastewater	4	266	1.65
Indust. wastewater	3	282	0.87

Table 3: NPOC results of typical samples
*Wastewater treatment plant inflow

the cellulose test. These are shown in Table 3. The typical wastewater treatment plant inflow (Figure 2) as well as the industrial wastewater samples investigated in this example (Figure 3) are comparable in terms of their RSD values and the peak shapes with samples without solid particles.

TOC-V_{CXN}: The multi-talent

Ideally, an analytical system will be used for only one analytical task. Meaning, one TOC system is designated exclusively for wastewater analysis. In daily laboratory practice this is usually impossible. A continuous alternation between different sample types such as ultra-pure and wastewater samples is obviously not realistic. Various limiting conditions such as sample pretreatment and the specific laboratory setup are some of the reasons. Nevertheless, application of the TOC-V series featuring a standard catalyzer is extensive. Using the integrated automatic dilution function, samples with a TOC-content of 25.000 mgC/L can be measured. The specific detection limit for these instruments is 50 µg/L. This enables application in wastewater as well as drinking water range – provided that the particular limiting conditions are observed and the sample series are processed separately from each other.

Figure 4 shows an NPOC calibration with a potassium hydrogen phthalate standard (DIN EN 1484) after several measurements of wastewater samples as well as suspensions.

In accordance with DIN 32645, this results in a detection limit of 18 µgC/L and the determination limit is 67 µgC/L.

This example shows that a regular TOC-V system featuring a standard catalyzer can also be operated effortlessly in the limiting range under realistic laboratory operating conditions.

Summary

The Shimadzu TOC-V_{CXN} system is an ideal and extremely reliable TOC analyzer for environmental analysis. This multi-talented system can easily handle the standard cellulose test as well as real wastewater samples. In addition, an extensive application spectrum in daily laboratory practice can be applied.

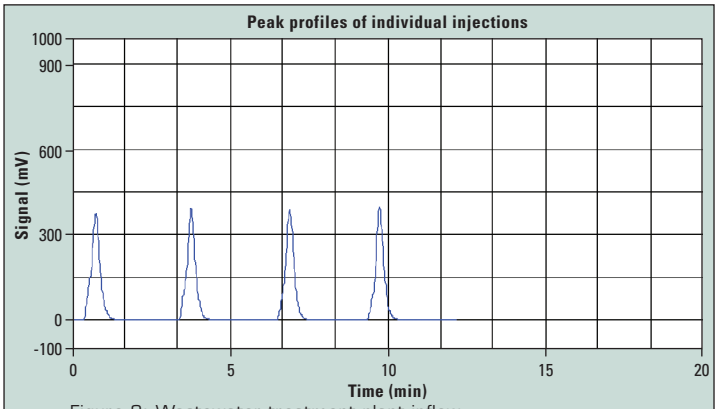

Figure 2: Wastewater treatment plant inflow

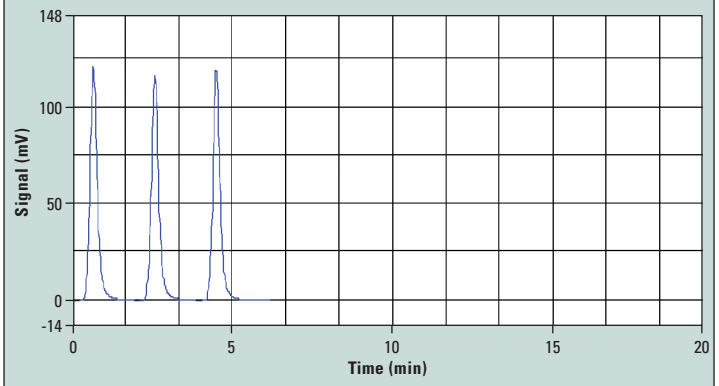

Figure 3: Industrial wastewater

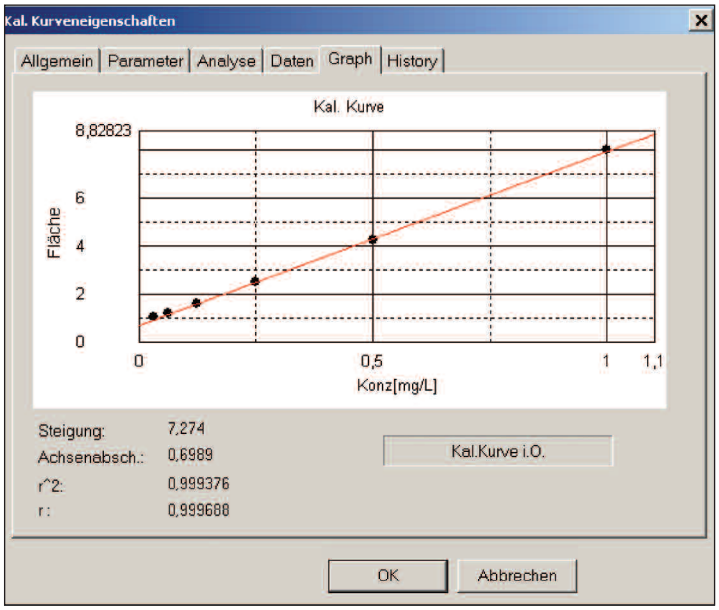

Figure 4: NPOC calibration