

# Sum parameters "on tra

## Continuous TOC determination in environmental analysis



Figure 1: TOC-4110 system

Identification of organic pollutants in wastewater is essential for performance evaluation, construction and operation of a wastewater treatment plant. Several parameters are currently used in wastewater analysis applications. Some of these are based on oxygen demand, for instance BOD (biochemical oxygen demand), COD (chemical oxygen demand and TOD (total oxygen demand). Using TOC analysis, however, the total organic carbon content is determined directly so the method is relatively free from matrix effects. The advantages of TOC analyses are apparent especially during continuous monitoring.

### Comparison of the sum parameters

#### BOD (biochemical oxygen demand)

The BOD value indicates the amount of oxygen in water needed for biological decomposition of organic compounds dissolved

in wastewater. For BOD determination, microorganisms are added to the water sample. After a pre-defined time interval, usually five days, the oxygen consumed by bacteria during decomposition of organic compounds in the water sample is determined.

The BOD<sub>5</sub> test is much too slow to provide suitable information and the results obtained are therefore not useful for monitoring and controlling of wastewater treatment procedures. For continuously operated BOD analyzers, determination within 5 - 15 minutes has been attempted.

#### COD (chemical oxygen demand)

The COD value indicates the amount of oxygen needed to chemically oxidize organic compounds present in wastewater. A chemical oxidizing agent is added to the sample and its consumption is subsequently measured. In addition to the organic compounds, other compounds (nitrites, bromides, iodides, metal ions and sulfur compounds) pres-

ent in the water sample can also be oxidized and have an influence on the measuring value.

The COD value is a subject of critical discussion due to the use of environmentally hazardous substances such as mercury and chromium compounds.

#### Total oxygen demand (TOD)

This rather seldom parameter evolved from the idea that chemical oxidation via COD could be replaced by thermal oxidation, whereby the amount of oxygen required for high-temperature combustion of all contaminants is determined. This reduces the measuring time when compared with COD determination. However, during TOD measurements, non-carbon containing compounds, for example sulfur and nitrogen compounds, are also oxidized. This is probably the reason why this parameter is not used by most well-known regulatory agencies.

#### TOC, total organic carbon

The TOC content is a measure of the concentration of organically bound carbon and is therefore a direct indication of the pollution levels by organic compounds in wastewater. For TOC determination, the sample is typically first acidified in order to convert the inorganic carbonate and hydrogen carbonate compounds into carbon dioxide. The dissolved CO<sub>2</sub> is subsequently removed from the sample via sparging with a stream of air. The remaining organic carbon compounds are then reconverted to CO<sub>2</sub> via high temperature (catalyst) or wet-chemical oxidation. The amount of CO<sub>2</sub> obtained is subsequently determined via NDIR detection. NDIR is a specific

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detection mode that renders TOC determination free from the effects described above when using other parameters. Based on this, the TOC parameter is used in many environmental regulations. Another advantage is the relatively simple conversion of TOC measurements into a continuous monitoring procedure.

#### Correlation between COD and TOC

In recent years, COD measurements are increasingly being replaced by TOC analysis. However, as the threshold values for organic pollution levels in wastewater are usually described and determined as COD values, efforts are underway to find a correlation between the two parameters. Based on the molecular mass ratio between oxygen and carbon, the theoretical correlation factor is 2.67. For real samples the correlation factor can lie between 2.5 and 4. This is due to the various analytical methods which are subject to different effects and interferences. During COD determination, when non-carbon components are also detected, the correlation factor will be greater than the theoretical value. When very stable carbon compounds are present in the sample and the oxidation power of the COD determination is not enough, the COD value will be less than the theoretical value. In addition the efficiency of detection of dissolution and particulate organically bound carbon should be considered as this can also affect the correlation factor between TOC and COD.

In order to simplify the determination of the correlation factor, paragraph 6 of the German wastewater law (AbwV) of June 17, 2004 includes the following: "One of the values for the chemi-

cal oxygen demand (COD) as defined in the wastewater regulatory law is, under compliance with paragraph 1, also valid when the four-fold value of the total organically bound carbon (TOC) in mg/L, does not exceed this value".

#### Continuous TOC determination

The fast and simple TOC determination enables the use of process-TOC analyzers for continuous monitoring of carbon pollution. In addition, there are many requirements for independent operation of a process analyzer. Shimadzu's TOC-4110 series offers numerous functions which allow customization for specific wastewater monitoring applications (Figure 1).

#### TOC-4110 system

The TOC-4110 is a high-performance TOC analyzer operating in catalytic combustion mode at 680 °C. Depending on the sample characteristics, it is possible to select one of three TOC analysis methods. The automatic dilution function enables TOC analyses up to 20,000 mg/L. In addition, a module for the measurement of total bound nitrogen (TN<sub>b</sub>) is available.

#### Sample preparation system

An analytical system is only as functional as the sample preparation procedure allows. For the TOC-4110 series, various sample preparation systems are available which can be tuned optimally to the individual application area.

In the single stream-option with homogenization, the sample enters the sample chamber via a strainer. A rotating knife homogenizes the sample before transferring it to the instrument for

further analysis. In this way, even samples containing large amounts of particulate matter can be measured without any problems.

After sampling, the chamber and the strainer are cleaned with rinsing water. Depending on the application, the rinsing water can be acidified in order to prevent growth of algae.

When several sample streams are to be measured using one instrument, the multi-stream sampler (Figure 2) can be used. Here also, the sample is homogenized prior to analysis. The rinsing function prevents sample carry-over effects when changing sample

streams. The measuring program can be individually selected for each sample stream. In addition, the user can freely choose the sequence by which the sample streams are to be measured.

The instruments can be started and calibrated from one measuring value. The same is true for the selection of different measuring streams. Numerous alarm and status signals simplify detection of exceeded threshold values and indicate maintenance requirements. An automatic dilution function and self-calibration option allow virtually independent operation of the instruments.

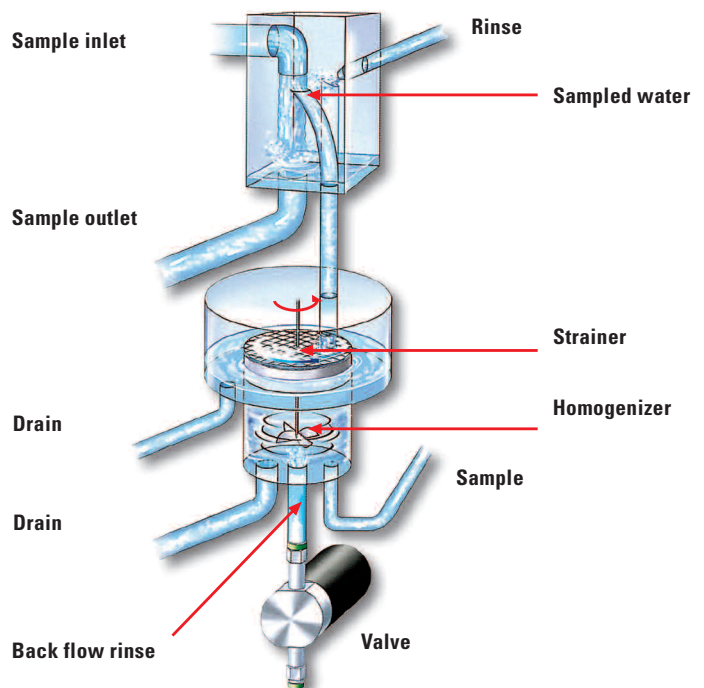


Figure 2: Multi-stream sampler with homogenization