



6. TOC process analysis

Laboratory analysis yields comprehensive and detailed results but, depending on circumstances, requires much time – time that is often not available during ongoing operations. For this reason, operators of different types of plants increasingly use sum parameters, which can also be determined continuously during the actual process. Contrary to conventional laboratory analysis, it is not an individual substance but an entire substance group that is determined here. In process waters from the chemical industry, sum parameters serve as an indicator of contaminations or all kinds of substance loads.

One of the most important chemical sum parameters is the TOC. It is a measure of the organic pollution level or the organic constituents in the matrix.

Particularly during process control it is important to obtain fast, continuous and

informative data on the organic pollution levels of waters. TOC process analysis offers this possibility. The sample is fed continuously to the instrument for subsequent measurement. The instrument sends the analytical data to the control room, which can react promptly to any possible process changes.

One of the most important attributes of a TOC process analyzer is its versatility. Since a TOC process system is not available 'off-the-shelf', each measurement task must be customized to the particular measuring problem, the matrix and the sampling location. The analyzer must be tailored to the specific measuring task and not vice versa.

Various types of sampling systems as well as kits and options for the many diverse applications are therefore essential. In addition to suitable equipment, robustness and service life of the instru-

ment (availability) are of major importance. After all, it is important that the analyzer can measure autonomously and transmit reliable analytical data.

With its TOC-4200 series, Shimadzu offers an online analyzer that, with its various modules, kits and options, provides exactly the flexibility needed and can be equipped for the most diverse applications. A selection of sampling techniques is available: from a single-stream sampler to a sample exchanger for six different sample streams, without or with homogenizer for water containing particles.

The TOC-4200 stands out not only in terms of its robustness but also by its reliability. The TOC-4200 already integrates the most advanced communication channels to the control room. In addition to the conventional communication modes, a Modbus communication

protocol is available. An optional web browser enables access to the instrument from any network-connected computer.

More information can be found in various application notes (for instance 'TOC determination in the paper industry, sewage treatment plants and power plants'). In addition to TOC process analysis, information is also available on the application areas 'Pharmaceutical industry', 'Chemical Industry', 'TOC special applications', 'TOC in daily practice' and 'Environmental analysis.'

Application News

No. SCA-130-601

Sum parameter – Total Organic Carbon

Continuous TOC/TN determination in wastewater treatment plants

A uniform definition of wastewater does not yet exist. Wastewater is often used as a generic term for sludge, industrial wastewater and infiltration water. The contents of wastewater can vary widely depending on their origin, and a distinction is made between oxygen consuming compounds, nutrients, harmful substances and contaminants [1].

Wastewater treatment is carried out to eliminate wastewater contents and to restore the natural water quality.



In municipal wastewater treatment plants, biological processes are used in aerobic and anaerobic wastewater treatment for the degradation of organically highly polluted wastewater. These plants use microbiological degradation processes. A stable nutrient ratio (carbon : nitrogen : phosphorus) is a precondition for an optimal degradation capacity of the microorganisms. Therefore, it is important to continuously monitor the inflow to the sewage plant. The treated effluent leaving the sewage plant must also be monitored continuously. Only when the limit levels of the German Wastewater Ordinance are reached, the water may flow back.

■ TOC determination in wastewater

Two oxidation techniques are now commonly used in TOC analysis:

- catalytic combustion, where carbon compounds are converted into CO₂ using a catalyst under high temperatures with subsequent detection of the resulting CO₂ using an NDIR detector
- wet chemical oxidation, which applies a combination of UV irradiation and persulfate for oxidation. The resulting CO₂ is either detected via an NDIR detector or using a conductivity detector.

For TOC determination in wastewater, catalytic combustion has become the method of choice based on its higher oxidation potential, especially for particles. Regarding TOC methods, the German Wastewater Ordinance states the following: "A TOC system with thermal-catalytic combustion (minimum temperature of 670 °C) must be used."

■ TOC-4200

The TOC-4200 is a high-performance analyzer with catalytic combustion at 680 °C. Depending on the sample characteristics, three TOC analysis methods can be selected (direct method, difference method, addition method). The automatic dilution function enables TOC analyses up to 20,000 mg/L. In addition, the TOC-4200 can be extended with a module for measuring the total bound nitrogen (TN). An automatic dilution function and the self-calibration option allow a virtually independent operation of the measuring system.

■ Sampling

An analysis system is only as good as the sample preparation preceding it. Various sample preparation systems are available for the 4200 series, which can be optimally tuned to the individual application area. When sewage plant inlet and outlet are to be measured using the same instrument, the sample stream switcher is used.

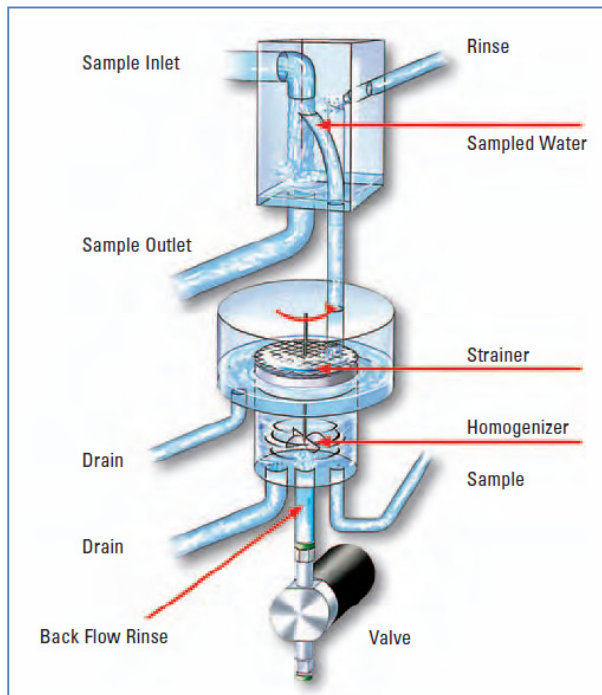


Fig. Multi-Stream switcher

The sample enters the sample chamber via a strainer, where it is homogenized through a rotating knife before it is transferred to the instrument for analysis. 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 the growth of algae. The rinsing function prevents any 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 measuring sequence of the sample streams.

■ Remote control

The measuring instruments can be started and calibrated from a control station, and a selection between the different measuring streams is possible. Numerous alarm and status signals simplify detection of exceeded limit levels and indicate the need for maintenance. In addition to the conventional communication modes, a Modbus communication channel is available. An optional web browser enables a 'view' of the instrument from any networked computer. The software counts consumables such as acids and pure water for dilution, and emits a signal to the measuring station for refilling the consumables.

■ Recommended analyzer / Configuration

TOC-4200

Multi-Stream suspended solids sampling unit
Acid Rinse option



[1] Source: Wikipedia

Application News

No. SCA-130-602

Sum parameter – Total Organic Carbon

TOC process analysis in the paper industry

Paper manufacturing requires the use of water for various processes (suspension and transport of the pulp, cooling water, sieve and felt cleaning, system cleaning). Although the water circulation in paper mills has been systematically optimized in recent years due to water conservation, the paper industry still requires large quantities of fresh water for the production of paper. Wherever fresh water is consumed, large amounts of wastewater are also produced and these must be continuously monitored. The wastewater from paper and pulp mills is usually highly polluted with organic carbon compounds. The many different products with various coatings, for instance specialty papers, produce wastewater of widely varying compositions and concentrations.



Fig.Example of four different sample streams in the paper industry

The online analysis of these types of wastewater is a major challenge for the analyzer and for the sample preparation



■ TOC-4200

The TOC-4200 is a high-performance analyzer with catalytic combustion at 680 °C. Depending on the sample characteristics, three TOC analysis methods can be selected (differential method, addition method, direct method). The automatic dilution function enables TOC analyses up to 20,000 mg/L. In addition, the TOC-4200 can be extended with a module for measuring the total bound nitrogen (TN).

An automatic dilution function and the self-calibration option allow a virtually independent operation of the measuring system. The measuring instruments can be started and calibrated from one measuring station and a selection between the different measuring streams is possible. Numerous alarm and status signals simplify detection of exceeded limit levels and indicate the need for maintenance.

In addition to the conventional communication modes, a Modbus communication channel is available. An optional web browser enables a 'view' of the instrument from any networked computer.

■ Sampling

The sometimes highly fibrous wastewater can clog tubes and pipes. Various mechanisms and options are available to prevent clogging. The wastewater streams are sequentially transported to the analyzer using various valves. Following each sample feed to the analyzer, the valves and tubes are flushed with fresh water and an acid rinse. This prevents the formation of buildup in the valves. The acid rinse and water rinse are controlled by the TOC analyzer.



Fig. Acid Rinse option to clean tubes and sampling system

After the sample has passed the respective valve, it enters the sample chamber via a strainer where it is homogenized using a rotating knife before it is transferred to the instrument for analysis. 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 acidified rinsing water.

The rinsing function prevents any 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 measuring sequence of the sample streams.

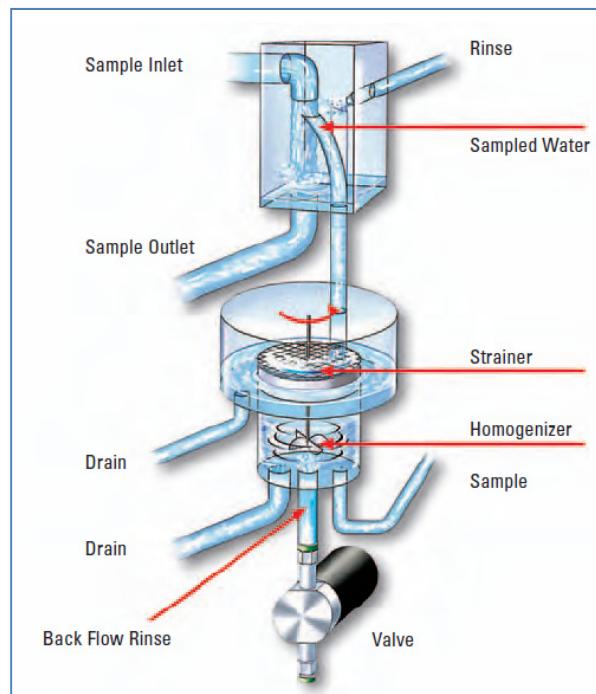


Fig.: Multi-stream suspended solids pretreatment unit

■ Recommended analyzer / Configuration

TOC-4200

Multi-stream suspended solid pretreatment unit

Acid rinse system

Application News

No. SCA-130-603

Sum parameter – Total Organic Carbon

Continuous TOC determination in the chemical industry

The high demand for many different products from the chemical industry and the required efficiency of the manufacturing processes often requires around-the-clock production. This results in huge amounts of wastewater. This water mostly originates from flowing water bodies.



Industrial wastewaters must be pretreated before being discharged into public sewage treatment plants. Direct discharge into water bodies requires an extensive cleaning process. This is why many large companies or industrial parks operate their own wastewater treatment plants.

■ TOC determination in industrial wastewater

The TOC content (Total Organic Carbon) is a measure of the concentration of organically bound carbon and is an indication of the pollution level by organic compounds in wastewater. This is why the TOC is often used in sewage treatment plants as measuring parameter to monitor and optimize the treatment process and to calculate pollution levels. The matrix in industrial effluents can vary greatly and can – prior to sewage treatment –

be polluted with high salt loads. For TOC determination in wastewater, catalytic combustion has become the method of choice based on its higher oxidation potential, especially for particles.

■ Are high salt loads a problem?

During thermal catalytic combustion of the test sample, the dissolved salts crystallize. High salt loads can lead to pollution of the catalyst, or even clogging of the system. Maintenance measures (for instance exchanging the catalyst) would then be required in order to render the instrument operational again. Of course, it is desirable to keep the maintenance intervals as long as possible.

■ TOC-4200

The TOC-4200 offers various possibilities to keep the maintenance needs for highly polluted samples at a minimum. The TOC-4200 with catalytic combustion at 680 °C is a high-performance analyzer. This temperature is lower than the melting point of sodium chloride and will, therefore, prevent deactivation of the active centers of the catalyst by a melt. The use of a platinum catalyst ensures the complete conversion of the organic compounds to CO₂. The highly sensitive NDIR detector allows small injection volumes (typically 20 - 50 µL) that reduce the absolute sample input onto the catalyst. A further reduction can be achieved using the integrated dilution function.

This can take place when measurement values are exceeded or can be applied permanently. In this case, the user specifies the desired dilution factor in the selected method.

■ Kit for high-salt samples

For the continuous TOC determination of samples with high salt loads (> 10 g/L), Shimadzu has developed a salt kit. The combustion tube has a special shape and uses two different catalyst beads. This combination prevents crystallization that can lead to clogging of the system.

■ TOC-4200 in daily practice

To verify the robustness and the reliability of the TOC-4200 during practical operation, the analyzer has been subjected to an endurance test in a German chemical park. For three months, the TOC-4200 had to stand the test under the most difficult conditions at one measuring station. The wastewater under investigation was alkaline ($\text{pH} \geq 12$) and highly saline (conductivity $4 \geq \text{mS/cm}$).



Fig. TOC-4200 on site

This is why the instrument was equipped with a kit for salt-containing samples. In addition, the automatic dilution function was used to dilute the samples (including the matrix).

The software enables planning of various automatic maintenance and calibration tasks. This way, automatic calibration of the measuring method was programmed to take place every 48 hours and automatic regeneration of the catalyst twice a week. Sampling took place in the counterflow mode with backflushing in order to prevent clogging.

■ Results of the practice test

As described in the test, a sample was collected every 4 minutes over a period of three months, and subsequently diluted, acidified and analyzed. After three months a total of approximately 27,000 measurements was achieved. Within this period, the instrument was automatically calibrated 45 times and the catalyst was regenerated nearly 25 times. These functions can be easily programmed via a calendar on the touch screen. The calibration function gradients remained stable over the entire time period.

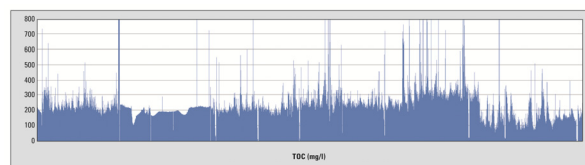


Fig. Diagram of 27.000 Measurement results (three months)

The test did not require any catalyst exchange or a single maintenance operation. There was also no instrument or software failure or any other component failure. In short: the TOC-4200 has successfully passed the endurance test.

■ Recommended analyzer / Configuration TOC-4200

Kit for high-salt samples

Application News

No. SCA-130-604

Sum parameter – Total Organic Carbon

Continuous condensate monitoring using the TOC-4200



The chemical and petrochemical industry uses superheated steam as energy carrier for the supply of energy needed in various thermal processing steps. Superheated steam is usually generated from ultrapure water, which prevents damage to the boilers. In order to use as little water as possible, the reflux condensate is redirected to the boiler. It is, therefore, important to ensure that the condensate is free from organic pollutants.

■ TOC determination in condensate

The TOC parameter provides information on organic pollution. The TOC can be easily determined and is easy to implement in process analysis. Two oxidation techniques are now commonly used in TOC analysis:

- Catalytic combustion, where carbon compounds are converted into CO₂ using a catalyst under high temperatures with subsequent detection of the resulting CO₂ using an NDIR detector
- Wet chemical oxidation, which uses a combination of UV irradiation and persulfate for oxidation. The resulting CO₂ is either detected via an NDIR detector or a via conductivity detector.

When applying TOC determination to condensates, few particles are usually expected, but here as well, it is better to be on the safe side with the higher oxidation potential offered by catalytic combustion. It is important to be able to quickly and reliably detect every possible organic contamination. Due to the low pollution level of the sample, the catalyst remains stable over a long time span, whereby the need for maintenance is relatively low.

■ TOC-4200

The high-performance TOC-4200 analyzer applies catalytic combustion at 680 °C. Three TOC analysis methods can be selected depending on the sample characteristics: differential method, addition method, direct method. Due to the automatic dilution function TOC analyses up to 20,000 mg/L are possible. In order to measure the total bound nitrogen (TN), the TOC-4200 can be extended with a specific module.



The self-calibration option and an automatic dilution function enable a virtually independent operation of the measuring system which can be started and calibrated from one measuring station. The different measuring streams can be selected.

Numerous status and alarm signals simplify detection of exceeded limit levels and indicate the need for maintenance. A Modbus communication channel complements the conventional communication modes. An optional web browser gives access to the instrument from any networked computer.

■ Sampling

For the 4200 series, various sample preparation systems are available, which can be optimally tuned to the individual application area. As condensates are homogeneous samples (in contrast to wastewater), an extra sample preparation step is not necessary. Two sampling systems are, therefore, suitable:

- an overflow tube, from which the sample is automatically drawn.
- filling the sampling chamber through a strainer (50 Mesh), in case the sample does contain particles that need to be removed prior to measurement. Compressed air empties the chamber and cleans the strainer.

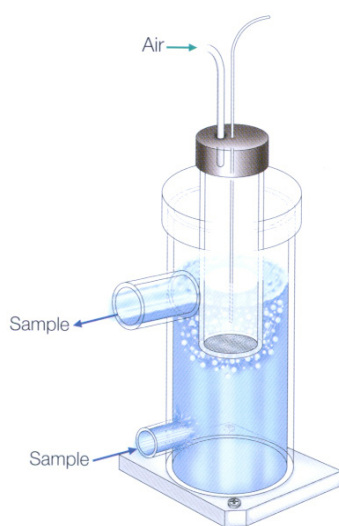


Fig. Sampling

■ TOC measuring method

TOC determination is often carried out via the NPOC method,

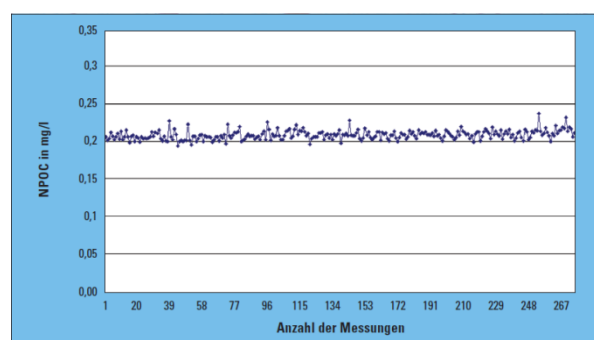
whereby the inorganic carbon content (carbonates and hydrogen carbonates) is removed prior to the actual analysis. For this purpose, the sample is drawn from the continuous sample stream into a syringe and automatically acidified via the 8-port valve (pH 2).

Using the sparging gas connection, the CO₂ formed (from the carbonates and hydrogen carbonates) is purged from the sample. The remaining solution containing the organic components is subsequently injected (septum-free) into the oxidation unit using the sliding valve technique. The syringe and 8-port valve allows automatic dilution and creation of calibration curves.

■ TOC measurement in the condensate

The system is calibrated using a 2-point calibration curve, blank water and 2 mg/L. This is realized using a standard catalyst and an injection volume of 200 µL. Typical measuring values are around 0.2 mg/L.

The measuring values of 275 consecutive measurements of a condensate monitoring are presented in the Figure below:



The mean value is 0.208 mg/L with a standard deviation of 0.006 mg/L. The results show that the required detection limit of 0.05 mg/L presents no problem.

■ Recommended analyzer / Configuration

TOC-4200

Backwash Strainer Sampling unit