

# 6. TOC process analysis





## 6. TOC process analysis

---

- 6.1. Continuous TOC/TN determination in wastewater treatment plants
- 6.2. TOC process analysis in the paper industry
- 6.3. Continuous TOC determination in the chemical industry
- 6.4. Continuous condensate monitoring using the TOC-4200
- 6.5. TOC-4200 with high sensitivity option
- 6.6. Continuous TOC determination on airports
- 6.7. TOC-4200 – measurement range up to 55,000 mg/L TOC
- 6.8. TOC-4200 – Carryover free TOC determination
- 6.9. Monitoring of cooling water with TOC-4200
- 6.10. Continuous TOC determination in Petrochemistry

---

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 instrument (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 CO<sub>2</sub> using a catalyst under high temperatures with subsequent detection of the resulting CO<sub>2</sub> using an NDIR detector
- wet chemical oxidation, which applies a combination of UV irradiation and persulfate for oxidation. The resulting CO<sub>2</sub> 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.

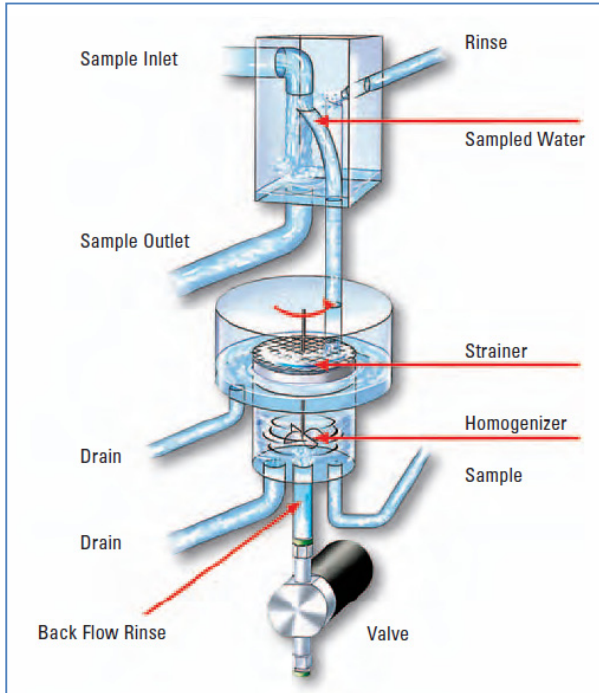


Fig. Multi-Stream switcher

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.

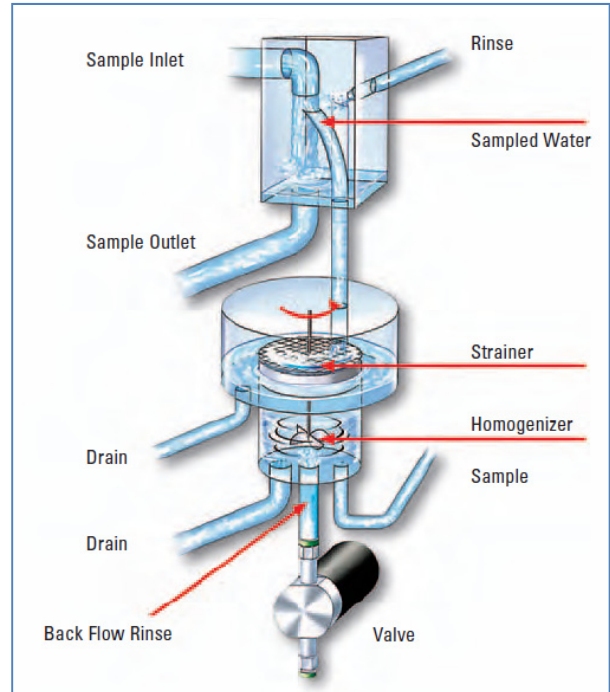


Fig.: Multi-stream suspended solids pretreatment unit

### ■ 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 CO<sub>2</sub>. 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 (pH  $\geq$  12) and highly saline (conductivity  $4 \geq$  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.

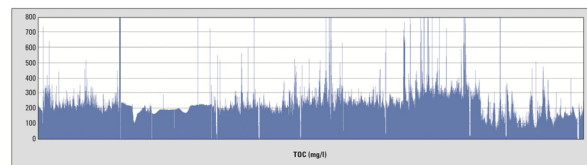


Fig. Diagram of 27.000 Measurement results (three months)

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 CO<sub>2</sub> using a catalyst under high temperatures with subsequent detection of the resulting CO<sub>2</sub> using an NDIR detector
- Wet chemical oxidation, which uses a combination of UV irradiation and persulfate for oxidation. The resulting CO<sub>2</sub> 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.

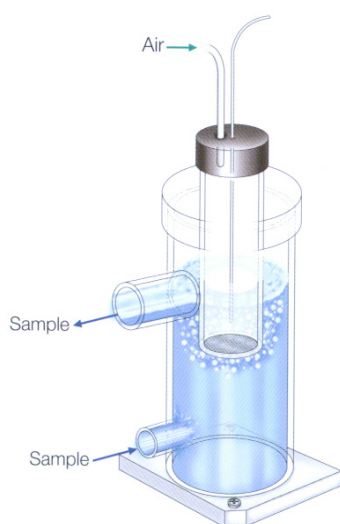


Fig. Sampling

### ■ TOC measuring method

TOC determination is often carried out via the NPOC method,

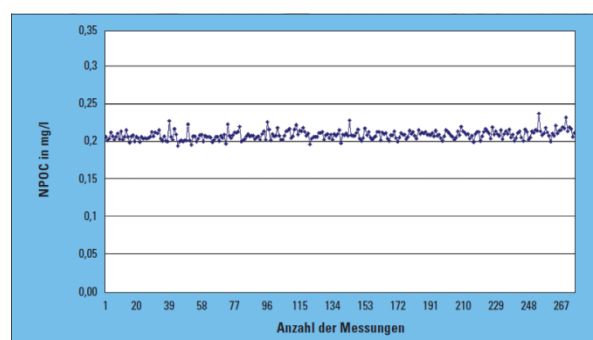
whereby the inorganic carbon content (carbonates and hydrogen carbonates) is removed prior to the actual analysis. For this purpose, the sample is drawn from the continuous sample stream into a syringe and automatically acidified via the 8-port valve (pH 2).

Using the sparging gas connection, the CO<sub>2</sub> 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

## Application News

**No.** SCA-130-605

Sum parameter – Total Organic Carbon

### TOC-4200 - High Sensitivity Measurement Option

Ultra pure water is one of the most widely used reagents in industry and its quality is therefore of utmost importance in all industrial processes. Quality control has, for many years, been carried out and documented via conductivity measurements, which provide an assessment of the concentration of all inorganic species present in water. This detection method does not take organic pollutants into account, as they typically do not contribute to conductivity. Organic pollutants can, however, greatly influence further industrial processes and it has become increasingly more important to include quantitative determination of all organic species in quality control of water samples.



#### ■ TOC (Total Organic Carbon)

The TOC value (Total Organic Carbon) can be used as a sum parameter for organic compounds. Similar to conductivity signals composed of various ionic compounds, the TOC value is a measure of the contribution of the numerous organic compounds present in a water sample.

When industrial processes require large volumes of ultra pure water, it is recommended to monitor its TOC content continuously.

#### ■ 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: difference 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<sub>b</sub>), 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.

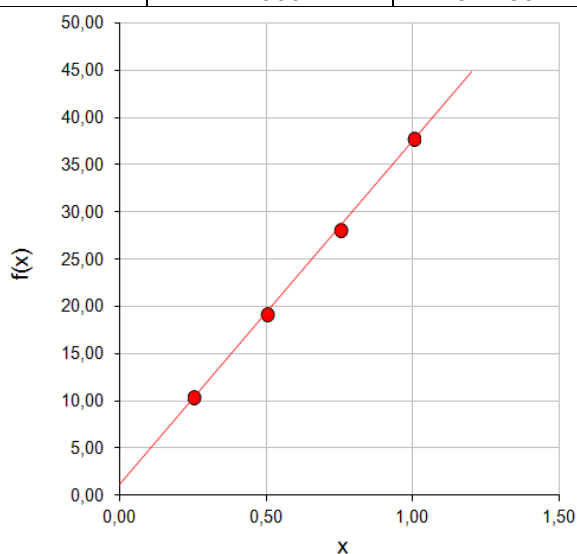
Numerous status and alarm signals simplify detection of exceeded limit levels and indicate the need for maintenance. A Modbus communication channel complements the conventional communication modes. An optional web browser gives access to the instrument from any networked computer.

### ■ High Sensitivity Measurement Option

Adding the high-sensitivity measurement option enables high-sensitivity measurements in the 0 to 1 mgC/L range FS. This option achieves high sensitivity by using a highly sensitive catalyst and increasing the maximum sample injection volume to 500 µL (standard specification is 150 µL).

### ■ Calibration Curve

Calibration Point	Concentration [mg/L]	Area counts
1	0.250	10.420
2	0.500	19.210
3	0.750	28.100
4	1.000	37.780



### ■ Calibration Curve Characteristics

Slope a: 36.88  
Intercept b: 1.135  
Correlation coeff r: 0.9997  
Result uncertainty: 33.33%  
Probability of error: 5%

Number of measurements n	3
Standard error of estimate Sy	0,333
Standard error of procedure Sx	0,009
Sum of squared deviations	0,313
Quantile (one-sided)	2,920
Quantile (two-sided)	4,303

### Analytical limits according to DIN 32645

Limit of detection	0,036	mg/L	
Limit of quantitation	0,142	mg/L	(approximation)
	0,137	mg/L	(exact)

### ■ Recommended analyzer / Configuration

TOC-4200

High Sensitivity Measurement Option

Carrier Gas: High-purity air or  
High-purity nitrogen,  
(N<sub>2</sub> Carrier Gas High  
Sensitivity Measurement  
Option required)

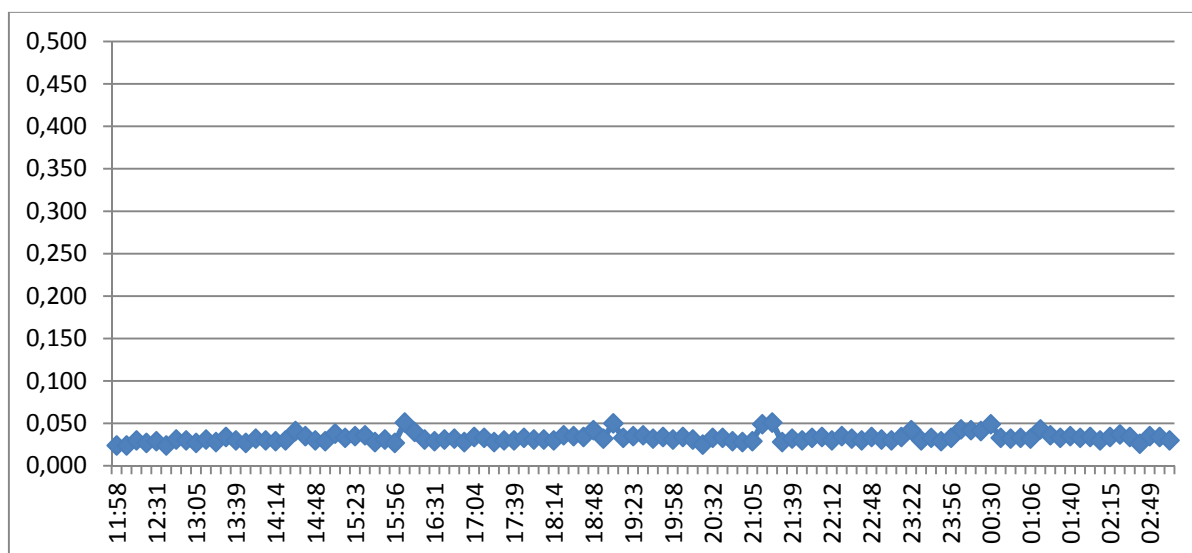


Fig. TOC-4200 Measurement results in mg/l of ultra pure water

## Application News

No. SCA-130-606

Sum parameter – Total Organic Carbon

### Continuous TOC determination on airports

Ice and snow on the wings of airplanes increase their total weight and have a negative impact on their aerodynamics. For reasons of safety, airplanes need to be de-iced just before they are ready for takeoff. The de-icing agent that is most frequently used is a mixture of water, glycol and additives. The exact composition depends, among other things, on the outside temperature.



After spraying the airplanes, the de-icing agent enters the sewage system where it leads to a significant increase of the organic load. Even when the agent used is biodegradable, the effluents must be subjected to a controlled treatment process. For the airport operator, it is therefore important to know the organic load of the airport's wastewater. The TOC sum parameter has been well established as an assessment parameter for wastewater analysis.

#### ■ Continuous online NPOC monitoring

Important for TOC determination is the differentiation between organic and inorganic carbon. Carbonates and hydrogen carbonates are, after all, present in all natural waters. The most widely used method for TOC determination is the so-called NPOC

method. In this method, the sample is acidified to convert the carbonates and hydrogen carbonates present in the sample to CO<sub>2</sub>. The resulting carbon dioxide is subsequently purged using a gas stream passed through the sample.

TOC (Total Organic Carbon) is a measure of the concentration of organically bound carbon and therefore reflects the pollution level of organic substances in wastewater.

Depending on the use of the de-icing agent, the TOC values can fluctuate significantly.

#### ■ Tried and tested and powerful – the TOC-4200

The TOC-4200 process analyzer is perfectly designed for this application. The TOC-4200 is a powerful analyser that uses catalytic combustion at 680 °C. After the analyser has automatically removed the inorganic carbon, a sub-quantity is injected onto a hot (680 °C) platinum catalyst. Here, all organic components present are oxidized to carbon dioxide. The resulting CO<sub>2</sub> is transported by a carrier gas stream to a highly sensitive and CO<sub>2</sub> selective NDIR detector, where it is measured. The TOC concentration is calculated using an external calibration.



The integrated dilution function enables TOC analyses up to 20,000 mg/L as well as automatic sample dilution when the measuring range is exceeded. The measured value is transmitted directly to a control room that initiates suitable measures when a threshold value is exceeded. The analyser can also take direct action. For example, a slider valve can be closed automatically to prevent the discharge of contaminated water into watercourses or stagnant water bodies.

#### ■ Multiple sample streams in one instrument

An airport may have several separate wastewater collection systems. In this case, multiple sample streams must be measured using one instrument, requiring the use of a multi-stream sampler. The sample is passed through a strainer and reaches the sample chamber where it is homogenised using a rotating knife before being transferred 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 strainer are cleaned with rinsing water. The rinsing water prevents carry-over effects

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

#### ■ Conclusion

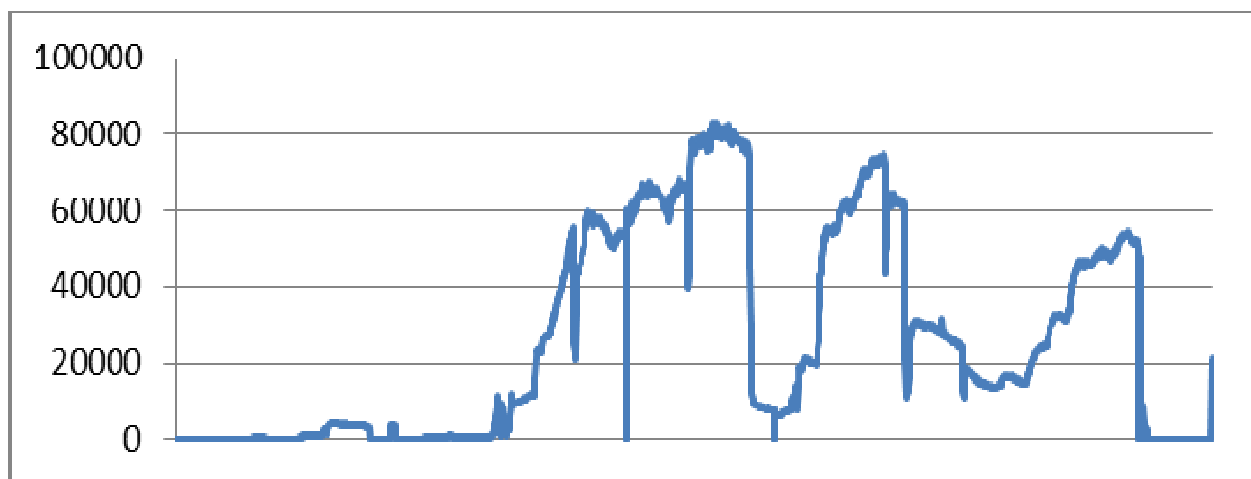
The automatic dilution function, the self-calibration check and the optimized sampling process allow virtually independent operation of the instrument at the airport. Numerous alarm and status signals simplify detection of exceeded threshold values or indicate maintenance requirements. In addition to the conventional possibilities, Modbus communication is available. An optional web browser enables access to the instrument from any networked computer. This makes the TOC-4200 the ideal instrument for continuous TOC determination of wastewater streams at airports, especially during the winter period.

#### ■ Recommended Analyser / Configuration

TOC-4200

Stand set

Multi-stream unit (for suspended samples)



The diagram represents measurement results of an airport wastewater stream in a period of 6 weeks. It shows the high fluctuation based on frosty or frost-free weather.

# Application News

Sum parameter – Total Organic Carbon

TOC-4200 -  
Measurements up to 55,000mg/L TOC

**No. SCA-130-608**

TOC-process analyzers (TOC-4200) are used in different applications from monitoring of cooling water or condensate up to high contaminated wastewater. For this, the TOC analyzers have to provide a broad measurement range.

### ■ ISP-Module in TOC-4200

The TOC-4200 achieves the broad measurement range by using the dilution function of the ISP-module (integrated sample pretreatment).

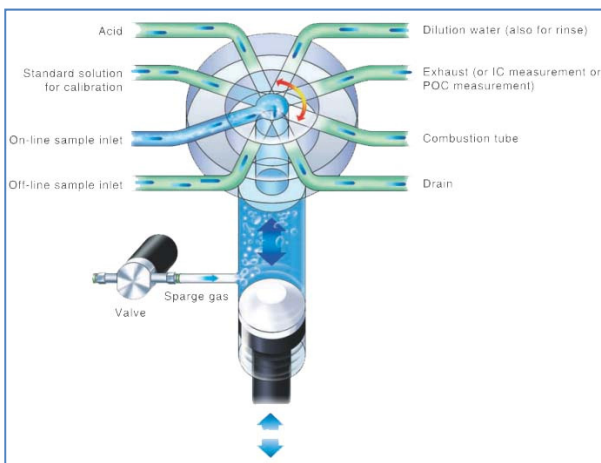


Figure: ISP-module in TOC-4200

The ISP module consists of an 8-port valve and a syringe with sparging gas connector. Sample and dilution water is taken in the right ratio into the syringe. The solution is homogenized by sparging (over the sparge gas connector) with carrier gas. Dilution factors from 2 to 50 can be used. Normally the announced measurement range of 20,000mg/L is sufficient for the controlling of wastewater. But in some application (e. g. de-icing process on airports) measurement values up to 50,000mg/L are possible.



### ■ TOC-determination in the range of 55,000mg/L

The recovery and repeatability in the high measurement range is proven with a Glucose solution.

#### Calibration

Parameter: TC  
Catalyst: Standard  
Std-Solution: 500mg/L (1-point)  
Injection vol.: 20µl

#Injection	Peak Area
1	768.6
2	784.2
3	762.1
Mean value	771.6
RSD	1,47%

#### Glucose standard

Std-Solution: 55,000mg/L  
Dil. factor: 40  
Injection vol.: 20µl  
Port: Offline-Port

#Inj.	Area	Concentration	Recovery
1	2106	54,595 mg/L	99,3%
2	2137	55,399 mg/L	100,7%
3	2104	54,543 mg/L	99,2%
<b>MW</b>	<b>2116</b>	<b>54,854 mg/L</b>	<b>99,7%</b>
<b>SD</b>	<b>18,51</b>	<b>479 mg/L</b>	
<b>RSD</b>	<b>0,87%</b>		

■ **TOC-Determination of a high concentrated Glycol solution**

TOC-determination on airports is one of the applications where the TOC values can fluctuate significantly depending on the use of the de-icing agent. The de-icing agent that is most frequently used is a mixture of water, glycol and additives.

Due to this, the test is repeated with a glycol solution in different concentration.

**1. Glycol Solution**

Parameter: TC  
Concentration: 45,250mg/L  
Dil. factor: 40  
Injection vol.: 20µl  
Port: Offline-Port

#Inj.	Area	Concentration	Recovery
1	1734	44,951 mg/L	99,3%
2	1770	45,885 mg/L	101,4%
3	1720	44,588 mg/L	98,5%
<b>MW</b>	<b>1741</b>	<b>45,133 mg/L</b>	<b>99,7%</b>
<b>SD</b>	<b>25,8</b>	<b>669 mg/L</b>	
<b>RSD</b>	<b>1,48%</b>		

**2. Glycol Solution**

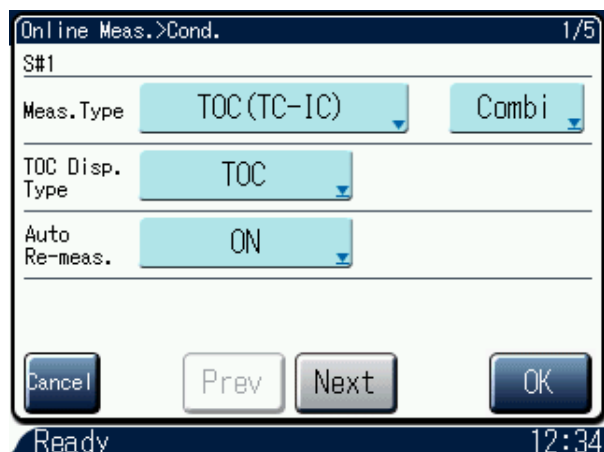
Parameter: TC  
Concentration: 55,340mg/L  
Dil. factor: 40  
Injection vol.: 20µl  
Port: Offline-Port

#Inj.	Area	Concentration	Recovery
1	2087	54,102 mg/L	97,8%
2	2087	54,102 mg/L	97,8%
3	2027	52,547 mg/L	95,0%
<b>MW</b>	<b>2067</b>	<b>45,133 mg/L</b>	<b>96,8%</b>
<b>SD</b>	<b>34,6</b>	<b>898 mg/L</b>	
<b>RSD</b>	<b>1,68%</b>		

■ **Function “Auto Re-measurement”**

The previous measurements are done with a fixed dilution factor of 40. But which parameter should be set if the samples with high concentration are exceptional cases only?

In this case, the TOC-4200 provides the function “Auto RE-measurement”.



This function allows setting of the parameters for the normal measurement (lower measurement range, un-diluted or low dilution factor).

If the measurement value exceeds the calibrated range, the injection volume and dilution factor are automatically updated and measurement is performed again.

■ **Conclusion**

The results show that the TOC-4200 can handle samples with very high concentration (up to 55,000 mg/L Carbon) without any problems

■ **Recommended Analyzer / Configuration**  
TOC-4200



## Application News

No. SCA-130-609

Sum Parameter – Total Organic Carbon

TOC-4200 – Carryover free TOC determination

The TOC (Total Organic Carbon) parameter for organic pollution of wastewater can serve as an indicator for accurate and efficient control of industrial processes. Using Shimadzu's TOC-4200 and switching between measuring points, up to six sample streams can be monitored – even in sample streams of different concentration levels.

### ■ Example: wastewater treatment plant

In industrial water purification and wastewater treatment plants, a variety of processes are used to purify wastewaters in different sub-processes (for instance, biological or filtration processes). The TOC sum parameter provides important information on the remaining organic contamination and thus on the efficiency of the treatment plant.



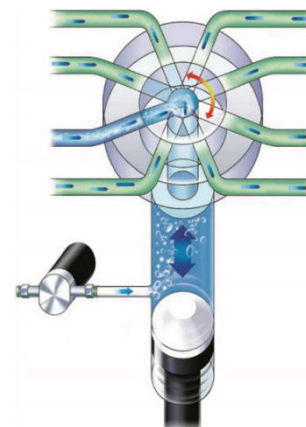
*Fig.: Example from paper industry:  
Four very diverse sample streams*

At the inlet of such plants, TOC concentrations of well over 1,000 mg/L as well as high salt loads can be expected. Dissolved organic substances are decomposed in biological intermediate stages. Flocculation or precipitation agents added at this stage modify the sample composition (matrix).

At the outlet of such purification or wastewater treatment plants, the TOC content of the effluent water is usually less than 50 mg/L. The sample matrices and measuring ranges of these sample streams thus vary widely. Monitoring these sample streams using a single analyzer will place high demands on the instrument and the sampling method used.

### ■ ISP-Module in the TOC-4200

The ISP module (Integrated Sample Pretreatment) is the heart of the TOC-4200 series. It consists of an 8-port valve and a syringe pump. The consistent use of inert materials reduces the risk of cross-contamination. In addition to automated sample pretreatment (acidification and sparging), the module enables dilution of the sample. It is also possible to determine self-cleaning sequences for the module as well as the sample inlets.



*Fig.: ISP-Module TOC-4200 Series*

The automated dilution function serves not only for measurement range extension, but also for matrix reduction. This reduces maintenance and lowers operating costs.

■ **Sampling method**

Incorrect measurement values often already occur due to carryover effects in the sample inlet line or in the sampler. Biological growth and deposits in the inlet line constitute a further risk of contamination. To minimize this, the sample should be directed to the sampler at a flow rate of higher than 1 m/s. Inspection openings and valves for manual or even automated flushing of the tubing should be provided for. The sampler should be constructed of inert materials. Automated rinsing steps between individual samplings further reduce time expenditure by the operator. To reduce problems during operation, it is important to pay particular attention to sampling during the project development phase.



■ **Practical test**

In a practical test, two sample streams with different matrices and TOC contents were analyzed. To demonstrate sample carry-over between these sample streams, they were alternately sampled and analyzed 90 times respectively.

Stream	S#1	S#2
Matrix	Pure water	3% NaCl-solution
Target conc.	1 mg/l	1000 mg/l
Parameter	NPOC	NPOC
Acid added	100µl	100µl
Inj. Volume	150µl	50µl
Dilution	None	Factor 10

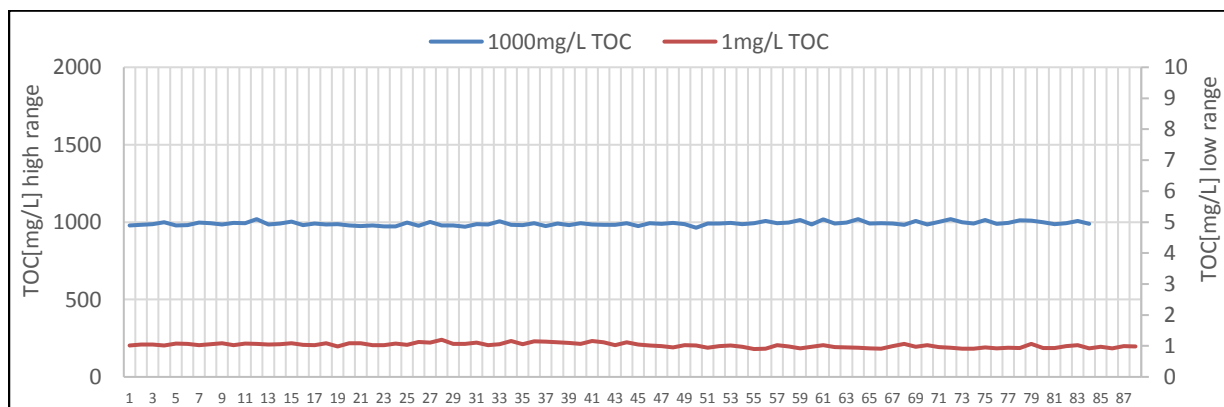
■ **Conclusions**

	S#1	S#2
Mean Value TOC (mg/l)	1,02	992,67
Standard deviation (mg/l)	0,07	13,32

Even with significant concentration and matrix differences between both sample streams, the TOC-4200 operated free from carry-over thanks to its inert construction and automated rinsing function.

■ **Recommended analyzer / Configuration**

TOC-4200  
Individual sampling system



## Application News

No. SCA-130-610

Sum Parameter – Total Organic Carbon

### Monitoring of cooling water with TOC-4200

Thermal power stations as well as the chemical industry use water as an energy carrier to dissipate heat in various processes. The heat energy of a process medium is absorbed by cooling water via heat exchangers.

The absorbed heat in turn is emitted by means of a cooling process. The cooling water is introduced either directly into a water body (continuous flow cooling), or cooled down by a cooling tower beforehand. Water which did not evaporate in the cooling tower is then being discharged (discharge cooling) or reused in the cooling circuit (closed circuit cooling).

Constant evaporation in the cooling circuit leads to an increase of salinity and to formation of carbonate scale, so that the water has to be diluted or exchanged regularly.



Usually cooling water is taken from a natural water body and purified by filtration systems. This avoids clogging of equipment and decreasing heat transfer rates.

Organic contaminants in the cooling water or fractured heat exchangers can cause reduced process efficiency and damage to the plant and the environment.

#### ■ TOC determination in cooling water

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 CO<sub>2</sub> using a catalyst under high temperatures with subsequent detection of the resulting CO<sub>2</sub> using an NDIR detector
- Wet chemical oxidation, which uses a combination of UV irradiation and persulfate for oxidation. The resulting CO<sub>2</sub> is either detected via an NDIR detector or via conductivity detector.

When applying TOC determination to cooling water, usually few particles are 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. The analyser availability is maximized by a combustion at temperatures below the melting points of common salts.

#### ■ TOC-4200

The high-performance TOC-4200 analyser applies catalytic combustion at 680 °C. Depending on the sample characteristics, the total inorganic carbon (TIC) and the volatile organic carbon (POC) can be measured in addition to TOC and TC. In order to measure the total bound nitrogen (TN), the TOC-4200 can be upgraded with a specific module.

An automatic dilution function and the self-monitoring of calibrations permit a largely independent operation of the analyser. From a remote control room the TOC-4200 can be started and calibrated. Additionally it is possible to select which sample stream is to be measured at which time. Versatile communication interfaces allow the registration of threshold limit values or maintenance requests.

#### ■ Sampling technique

Various sample preparation systems, which can be matched optimally to the scope of application, are available for the TOC-4200. Temperature and pressure resistant stainless steel is an ideal choice for the sampling of cooling water. A counter-flow type sampling mechanism is a good choice in this case:

It consists of a stainless-steel pipe bend, into which a sampling capillary is inserted. The TOC-4200 draws the flowing sample against its direction of flow through the capillary. After sampling, the capillary is rinsed backwards with water.

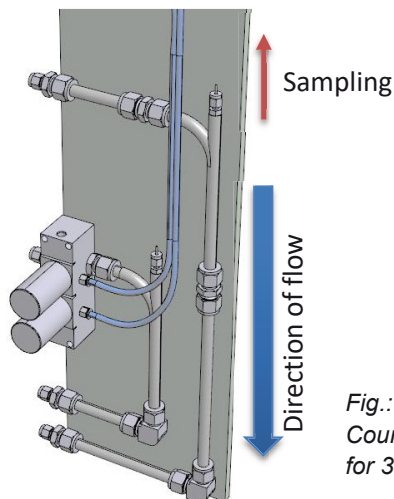


Fig.: Counter-flow sampler for 3 streams

This way the sampling device does contain as less moving parts or filters as possible and requires low maintenance effort. When no sample is taken, the flowing sample carries particles away from the capillary so that no clogging occurs.

The number of sample streams the TOC-4200 monitors, can be optionally extended to a maximum of six.

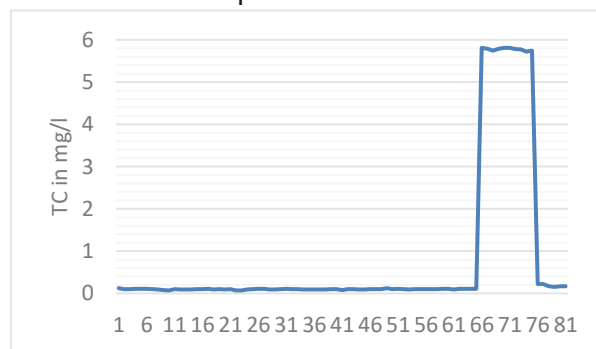
#### ■ Measurement method

The TC method is often used for the monitoring of cooling water. In this case the sum of organic (TOC including POC) and inorganic (TIC) carbon compounds is determined.

For this purpose, the sample is drawn with a syringe pump from the continuous sample stream and then injected into the oxidation unit using a septum-free slider mechanism. Using TC analysis with its low cycle times of 2-3 minutes allows for a very fast process adjustment. The dilution function of the syringe pump enables dynamic expansion of the measurement range so that exact values are obtained even if a heat exchanger ruptures. No additional detectors are necessary for this.

#### ■ TC response behavior

A TOC-4200 was calibrated to a measurement range of 10 mg/l. A sample with a TOC content of 0.1 mg/l is continuously analyzed until a sudden contamination up to 6 mg/L TOC is added to the sample.



The average cycle time is 2:38min at mean values of 0.098 mg/l for normal load and 5.78 mg/l for burst contamination.

#### ■ Recommended analyser / Configuration

TOC-4200

Counter-flow type sampling mechanism

The natural resource of petroleum is an integral part of our modern economy. It is used not only as a source of energy, but also as raw material for countless products such as plastics, textile fibers, detergents, colorants, fertilizers or pharmaceuticals.



In petroleum refineries, purified and deionized crude oil is preheated and then separated into its constituents in rectification columns. Fractions created by this process are further refined, or redistilled.

#### ■ Requirements to modern refineries

In many cases only so-called "cracking" of long-chain hydrocarbons allows the market to be covered by crude oil. The purity of the resulting products, for example low-sulfur fuels, is subject to high quality requirements, which leads to a corresponding complexity of process technology. The generation of steam for heating material flow is an important and energy-consuming process, which in turn also has the largest energy saving potential. Corrosion on equipment such as heat exchangers and boilers, leads to reduced energy efficiency and contamination of the backflow condensate, so that it must be replaced and cleaned. This results in high costs for the plant operator.

#### ■ Environmental protection

Sewage and surface waters arising in a refinery contain environmentally harmful compounds which may be dissolved and undissolved. Non-dissolved components such as oils and solids are often eliminated prior to cleaning by means of gravitational separation. Usually dissolved compounds are degraded by biological processes. However, biological purification plants are sensitive to the nature and amount of influent organic impurities. In order to prevent a reduced cleaning performance, biological collapse of the plant, or even a pollutant input into the environment, it is of utmost importance to continuously monitor the refining effluents.

#### ■ TOC-4200

The high-performance TOC-4200 analyser applies catalytic combustion at 680 °C. The powerful oxidation allows complete and rapid detection of both dissolved and undissolved compounds, and enables the direct detection of all contained hydrocarbons. Depending on the sample characteristics, the total inorganic carbon (TIC) and the volatile organic carbon (POC) can be measured in addition to TOC and TC. In order to measure the total bound nitrogen (TN), the TOC-4200 can be upgraded with a specific module.

The consistent usage of inert materials reduces the risk of cross-contamination through the absorption and desorption of oils and fats. All fluid paths, including the sample supply line, are additionally purged and rinsed between each measurement.

The automatic dilution function enables the extension of the analyser's measuring range, as well as the reduction of sample matrix. This reduces maintenance effort and as such the running costs for the operator.

#### ■ Sampling technique

Taking a representative sample is the first and most important step for accurate TOC analysis. Oil and fat in particular can be present in water in very different forms: as oil film, emulsion, particles or whole chunks, or generally speaking as a multi-phase mixture.

Phase separation before sampling should be avoided so that the sum of all organic contaminants can be detected. Ideally, the sample is taken from a section of turbulent flow where good blending predominates. High pressures and flow rates in the sample line favour the stability of the mixture.

Under these conditions, the use of a counter-flow type sampling mechanism, in which the sample is taken directly from the flowing medium without filtration, is recommended.

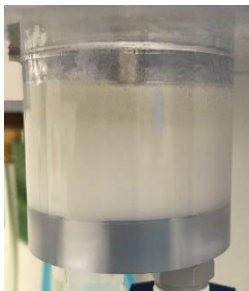


Fig.: Mechanically created emulsion

If the sample is a multi-phase liquid, but not available in turbulence and at high pressure, it is recommended to create an emulsion. The addition of emulsifiers, or more specifically surfactants, is not a suitable method here however.

Surfactants are detected as TOC and lead to false-high readings.

Mechanical emulsification of the sample by high-speed stirring is recommended instead. By this method oil and fat droplets can be crushed and dispersed in water. For TOC determination, this only temporarily stable mixture is injected immediately after its creation. Longer dwell times that could lead to the breaking of the emulsion, with the effect of false-low readings, are thus avoided.

#### ■ Installation site

Generally, the distance between the sampled material stream and the TOC analyser should be kept as short as possible to prevent longer response times by larger transport time. In refineries however, explosion-hazard areas can limit possible installation sites for a combustion analyser.



Fig.: TOC analyser in pressurized cabinet

For this purpose, the TOC-4200 can optionally be equipped with a pressured enclosure (Ex p) for zone 1 or 2. Versatile communication interfaces also allow monitoring and control of the analyser without opening the Ex housing.

#### ■ Recommended analyser / configuration

TOC-4200

Individual sampling system

Optional enclosure for zone 1 or 2