

# TOC Application Handbook



# Content

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## **1. Environmental Analysis**

- 1.1. TOC determination in drinking water
- 1.2. TOC determination in wastewater
- 1.3. TOC determination in surface water and groundwater
- 1.4. TOC determination in seawater
- 1.5. TOC determination in solid samples using the suspension method
- 1.6. TOC determination in particle-containing samples – Cellulose test according EN 1484
- 1.7. Determination of particulate organic after filtration (glass fiber suspension)

## **2. Pharmaceutical Industry**

- 2.1. TOC determination in ultrapure water – comparison of the various oxidation techniques
- 2.2. TOC determination in cleaning validation – Final Rinse
- 2.3. TOC determination in cleaning validation – SWAB Method
- 2.4. TOC determination according to EP 2.2.44

## **3. Chemical Industry**

- 3.1. TOC determination in hydrochloric acid
- 3.2. TOC determination in nitric acid
- 3.3. TOC determination in sulfuric acid
- 3.4. TOC determination in brine solution
- 3.5. TOC determination in sodium hydroxide solution
- 3.6. TOC determination in soda solution
- 3.7. TOC determination in ammonia or ammonium salt solution
- 3.8. TOC determination in sodium nitrate and sodium nitrite

## **4. TOC special application**

- 4.1. TOC determination in algal biomass – suspension method
- 4.2. TOC-Determination in liquid manure and fermentation fluids – suspension method
- 4.3. Carbon dioxide determination in beer

## **5. TOC in daily practice**

- 5.1. TOC determination methods according to EN 1484
- 5.2. Determination of the purgeable organic carbon (POC)
- 5.3. TN<sub>b</sub> – total bound nitrogen
- 5.4. Kit for high-salt samples
- 5.5. Kit for small sample volumes
- 5.6. Kit for manual injections
- 5.7. Calibration with automatic dilution function
- 5.8. Blank value consideration in TOC analysis
- 5.9. TOC – Measurement principle – catalytic combustion at 680°C

## **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





# 1. Environmental analysis

A clean environment is the basis for a healthy life. Whether water, soil or air – keeping the environment clean for the protection of all creatures should be the primary responsibility of any society. In Europe alone, there are numerous laws, ordinances and administrative regulations describing the environmental conditions needed to ensure a certain environmental standard. Instrumental analysis is a useful tool to measure the status of environmental conditions.

Looking at the numbers of possible chemical contaminations (compounds), the group of organic compounds is the largest. With an estimated number of more than 19 million, it is impossible to detect and quantify each and every one of them.

The sum parameter TOC (Total Organic Carbon) is one of the most important

parameters used in many environmental applications. TOC analysis enables the determination of the sum of all organically bound carbons in the above-mentioned organic compounds and is, therefore, a measure of organic pollution in a matrix.

The relevance of the TOC parameter becomes clear when looking at the parameter lists of various regulations in European countries: the Waste Disposal Ordinance, the Waste Technical Guidelines, the Landfill Ordinance, the Ordinance pertaining to the Recovery of Waste, the Stoving Directive, the Drinking Water Ordinance and the Wastewater Ordinance are just some that mention TOC as a valuable parameter.

TOC analysis is therefore carried out in a wide variety of environmental matrices: from groundwater to seawater, from

drinking water to wastewater, from soils to sewage sludge. The diversity in environmental applications creates many different challenges for the analytical systems being used. In addition to the different concentration ranges, TOC analysis repeatedly faces different types of conditions such as salt content or number of particles.

Shimadzu offers various solutions for these different applications. The TOC-L family is module-based. Two basic analyzer types can be equipped with many options, kits and numerous accessories and customized to any particular application. This makes the TOC-L one of the most universal TOC analyzers.

Further details can be found in the individual application notes (for instance 'TOC determination in drinking water, wastewater or suspensions').

In addition to environmental analysis, there are also application notes and information on 'Pharmaceutical industry', 'Chemical Industry', 'TOC special applications', 'TOC in daily practice' and 'TOC process analysis.'

## Application News

No. SCA-130-101

Sum parameter – Total Organic Carbon

TOC –Determination in drinking water

Drinking water is one of the main important and life-sustaining food stuffs and is essential to the survival of all known organism. It is a crucial component for metabolic processes and serves as solvent for many bodily solutes. Water for human consumption must be free from pathogens, pleasant to drink and pure. Continuous monitoring is carried out according to European Drinking Water Regulation to ensure the greatest possible security



### ■ European Drinking Water Directive

The Directive is intended to protect human health by laying down healthiness and purity requirements which must be met by drinking water within the European Union (EU).

The directive applies to all water intended for human consumption apart from natural mineral waters and water which are medicinal products.

The European drinking water directive includes the category of indicator parameter value specifications. These are not directly linked to health problems but have an indicator function.

This list of indicator parameters also includes the TOC value (total organic carbon), which has not been assigned a limiting value or criterion but can be considered as a cautionary warning for action under unusual circumstances. Another indicator parameter included in the list is oxidizability. This is a measure for the sum of all chemically oxidizable organically bound compounds present in water.

With reference to drinking water limiting values, this parameter is no cause for direct health concern but can lead to regermination or undesirable disinfection byproducts. Oxidizability is proportional to the sum of organically bound carbons that are determined as DOC (dissolved organic carbon) or TOC. Oxidizability can therefore be replaced by the TOC parameter. The frequency of determination of the parameter indicators depends on the volume of water that is produced or released in a water supply area.



### ■ TOC determination in drinking water

When examining carbon compounds in drinking water, it is apparent that the amount of inorganic carbons, such as carbonates and hydrogen carbonates, is much higher than the organic fraction.



The organic fraction is only 1% of the total carbons. A TOC determination via the difference method ( $TOC = TC - IC$ ) will not be appropriate in this case, as the calculated TOC value is prone to large statistical errors.

**Example:**

$$TC = 100 \text{ mg/l (RSD = 2\%)} \pm 2 \text{ mg/l} \\ (98 - 102 \text{ mg/l})$$

$$IC = 98 \text{ mg/l (RSD = 2\%)} \pm 1,96 \text{ mg/l} \\ (96,04 - 99,96 \text{ mg/l})$$

Based on error propagation the total error is  $\pm 3,96 \text{ mg/l}$

$$TOC \text{ (calc.)} = 2 \text{ mg/l} \pm 3,96 \text{ mg/l} \\ (- 1,96 - 5,96 \text{ mg/l})$$

The total error is bigger than the TOC-result, negative results are possible.

According to European Standardization EN 1484 (instructions for the determination of total organic carbon and dissolved organic carbon), the difference method can only be applied when the TIC value (total inorganic carbon) is smaller than the TOC value.

For drinking water analysis the NPOC method (non purgeable organic carbon) is therefore used. The drinking water sample is first acidified to a pH value of 2. This way the carbonates and hydrogen carbonates are transformed into carbon dioxide. The  $CO_2$  is then removed via sparging with carrier gas. The amount of volatile and therefore purgeable organic carbon can be disregarded in drinking water. What remains is a solution of non-volatile organic carbon compounds. These can be oxidized to  $CO_2$  and detected via NDIR.

■ **TOC-L Series**

The sample preparation for the NPOC method (acidification and sparging) is automatically done in the TOC-L analyzer. The removing of the TIC can be performed either in the syringe of the ISP-Module or in the autosampler with the external spare kit.

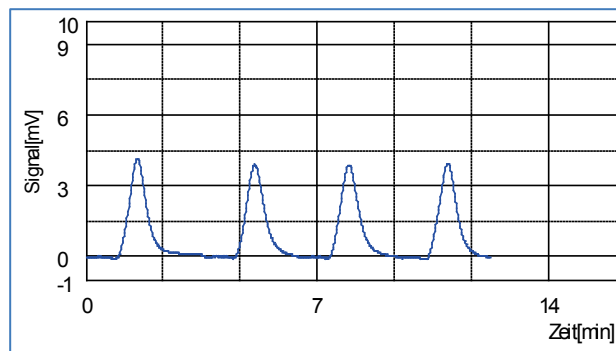
The ISP (integrated sample preparation) module consists of an 8-port valve and a syringe with sparging gas connection. In addition to acidification and sparging in the syringe, the ISP also enables automatic dilution. This feature facilitates an extended measuring range, dilution of highly contaminated samples and the preparation of a series of calibration samples from a stock solution. The ISP module can therefore considerably reduce time-consuming sample handling steps.

■ **Example of drinking water analysis:**

NPOC-Method

Acidification: 1,5%

Sparge time: 5 minutes



■ **Recommended analyzer / Configuration**

TOC-L<sub>CPH</sub>

ASI-L (40ml), External Sparge-Kit.

TOC-V<sub>WP</sub> with ASI-V (40ml)

# Application News

**No. SCA-130-102**

Sum parameter Total Organic Carbon

## TOC – Determination in wastewater

Wastewater is water that has been contaminated by use. In terms of its composition, wastewater is not homogeneous but as diverse as its possible sources.



According to the German Water Resources Act (Wasserhaushaltsgesetz, WHG) wastewater is defined as follows:

“Wastewater is

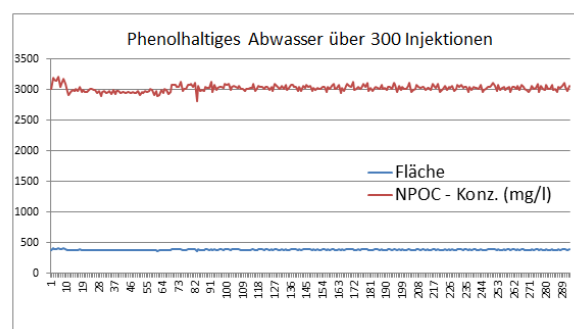
- 1) water whose properties have been changed by domestic, commercial, agricultural or other use and the water (sewage) discharged with it during dry weather conditions as well as
- 2) the run-off and collected water (rainwater) from built-up or paved areas following precipitation.

Sewage also includes the liquids that are discharged and collected from waste treatment and storage plants”.

This diversity of wastewaters should also be taken into account during the analysis. Wastewater can thus contain small amounts of organic pollutants with little matrix, as well as highly saline products with high amounts of organic components.

### ■ Example of wastewater measurement

Below, a strongly saline wastewater from the chemical industry was analyzed. In addition to various substances present in low amounts, the wastewater mainly contained high amounts of phenolic substances originating from production processes.



	Fläche	NPOC (mg/l)
Mittelwert	381,1	3024
Standardabweichung abs.	6,6	51,8
Standardabweichung in %	1,7	1,7

Fig. Result of the wastewater



A TOC-L<sub>CPN</sub> was used for the analysis. To ensure efficient use of the instrument for large sample quantities, the fully automated dilution function and the additional high-salt sample kit were applied. With a dedicated function, samples could be diluted up to a factor of 1:50. For the phenol-containing wastewater, the sample was diluted by a factor of 1:10. The high-salt sample kit increases the lifetime of the catalyst for high salt loads.



Fig. Combustion tube (of salt kit) after the long term test

To test long-term stability, more than 300 injections of the saline wastewater were compared.

The graph shows the stability of measurement of over 300 injections with a standard deviation of 1.7%. Mean value was 3042 mg/L.

In many cases, wastewater contains particles. Where the wastewaters are not filtered, the particles need to be held in suspension by stirring. In order to prevent inhomogeneity of the particles by sedimentation within the syringe body, multiple injections from the same syringe may not be carried out in this case.



■ **Recommended Analyzer / Configuration**

TOC-L<sub>CPN</sub> with normal sensitive Catalyst or kit for high salt samples (B-Type-Scrubber) ASI-L (40ml) with stirrer option (for samples with particles) and External Sparge-Kit

■ **Useful instrument parameters::**

- Use of integrated dilution function for automated sample dilution
- In the presence of particles: deactivation of multiple injection via the syringe.

# Application News

**No.** SCA-130-103

Sum parameter Total Organic Carbon

## TOC –Determination in surface and groundwater

The German Water Resources Act (Wasserhaushaltsgesetz, WHG) serves the purpose of “sustainable water management to protect waters as a component of the ecological balance, as a basis of human existence, as a habitat for animals and plants as well as a usable good”. The various water types are defined in this act.



### ■ Definitions according to WHG

Groundwater is defined as “water that is below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil”. Surface water is “permanently or temporarily confined flowing or standing waters, and unconfined waters from natural springs”. Surface waters include bodies of water above ground such as lakes, rivers and streams as well as coastal waters. Rainwater that has not yet flowed away is also included.

Surface waters are often contaminated with particles and harmful substances. They can only be used as drinking water after undergoing a treatment process (Wikipedia). By definition, these waters can be very different due to regional conditions. They can

exhibit high levels of TOC concentrations caused by natural substances or dissolved harmful substances from the environment.

Surface water	Typical TOC-Concentrations in mg/l
Clean spring water	1 - 2
Weakly polluted rivers and streams	2 – 5
Nutrient-rich stagnant lakes	5 - 10
Polluted waters	50 - >100
Clean groundwater (well water)	1 -2

Typical TOC-Concentrations (1)

Depending on the region, high TIC concentration (> 100 mg/L) can also occur in surface water as well as in groundwater.

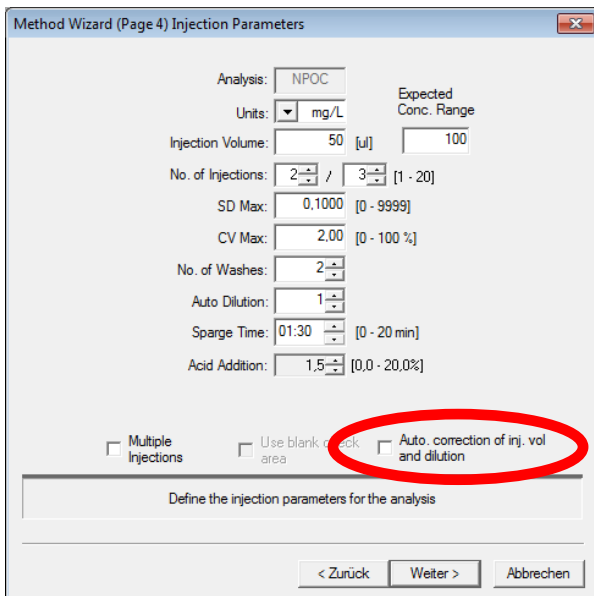
At TOC concentrations of far below 10 mg/L, it needs to be ensured that inorganic carbon is being purged from the solution.



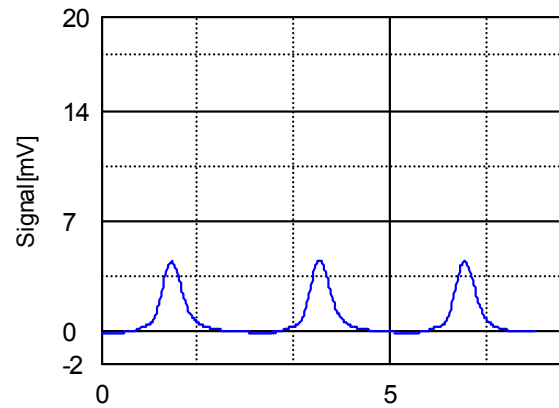
### ■ TOC-L

To prepare the sample accordingly, the ISP module of the TOC-L automatically acidifies the sample and strips the CO<sub>2</sub> originating from the TIC.

The excellent particle tolerance of the analyzers enables analysis of particle-containing surface waters. Using the automatic dilution function, multi-point calibrations can be generated from a single standard. In the investigation of unknown surface waters or groundwater, one of the samples may exceed the calibration range. In this case, the TOC Control-L software offers an option for automatic dilution to bring the sample back within the calibration range.



### ■ Example: River water



NPOC-Method

Acidification: 1,5%

Spurge-time: 5 Minutes

TOC-Concentration: 3,4 mg/l

RSD (3 Injections): 1,4%



### ■ Recommended analyzer / Configuration

- TOC-L<sub>LCPH</sub>
- ASI-L (40ml) with stirrer option
- External Spurge-Kit

(1) Source: Wikipedia

## Application News

**No.** SCA-130-104

Sum parameter – Total Organic Carbon

TOC – Determination in seawater

TOC is an important indicator of the degree of organic contamination. TOC determination is used extensively to detect and study environmental and seawater pollution. In recent years, increased attention is being paid to the measurement of the nitrogen compounds (TN = Total Nitrogen) responsible for eutrophication.



### ■ Seawater samples

Seawater has an average salinity of 3.5% mass fraction. The total salinity fluctuates depending on each ocean. The Baltic Sea has a salinity of 0.2 to 2%. Some inland seas without outlets have far higher water salinities. The Dead Sea is known for its salinity of 28%. Chloride ions constitute the main component of the anions, followed by sulfate ions. Sodium ions dominate among the cations, which is why the major proportion of crystallized sea salts consists of sodium chloride (common salt). Magnesium, calcium and potassium ions are represented in smaller amounts.

### ■ Are high salt loads a problem?

During thermal catalytic combustion of the test sample, the dissolved salts crystallize. Depending on the salt concentration, this can affect or clog 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-L Series

The TOC-L series offers various possibilities to keep the maintenance need for highly polluted samples as low as possible. The analyzers are operated under catalytic combustion at 680 °C. This temperature is lower than the melting point of sodium chloride and therefore prevents deactivation of the active centers of the catalyst by a melt. The use of the platinum catalyst ensures complete conversion of organic carbon compounds to CO<sub>2</sub>.

The highly sensitive NDIR detector allows small injection volumes (typically 20 - 50 µL) that reduce absolute sample input onto the catalyst.



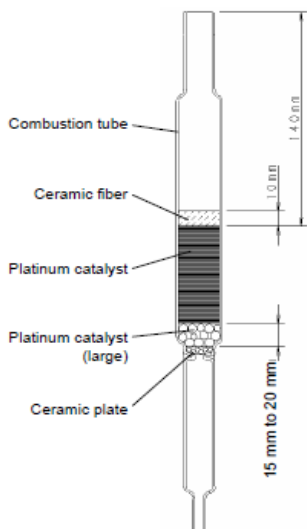


### ■ Kit for high-salt samples

The TOC-L series features a kit for high-salt samples, which significantly increases instrument availability.

Using this kit in a seawater application, it was possible to carry out 2500 injections without maintenance (injection volume of 40 µL).

The kit consists of a combustion tube with a special geometry and a unique catalyst mixture.



In this application, sample acidification is carried out with sulfuric acid which is used to modify the sample matrix. While NaCl has a melting point of 801 °C, the melting point of NaSO<sub>4</sub> is higher (888 °C). The potassium salts of sulfuric acid also have a significantly higher melting point than those of hydrochloric acid. This has a positive effect on the lifetime of the combustion tube.

Compound	Melting point
NaCl	801°C
KCl	773°C
Na <sub>2</sub> SO <sub>4</sub>	888°C
MgCl <sub>2</sub>	708°C
CaCl <sub>2</sub>	782°C
K <sub>2</sub> SO <sub>4</sub>	1.069°C

Tab. Melting point of different salts

### ■ Simultaneous TN determination using the TNM-L

Based on the similar oxidation process, the TNb determination can be carried out simultaneously with the TOC measurement. For this application, the TNM-L option is installed on the main TOC-L system.

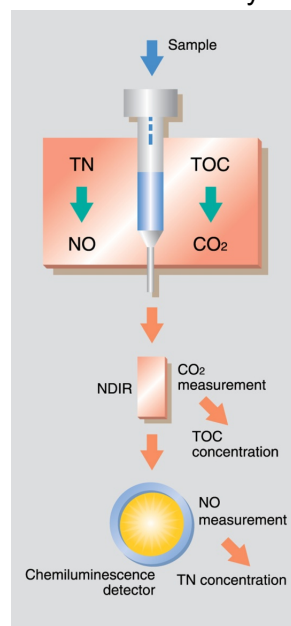


Figure: Simultaneous TOC/TN-Determination

### ■ Recommended analyzer / Configuration

TOC-L<sub>CPN</sub>  
ASI-L (40ml), External Sparge-Kit.  
Kit for high-salt samples  
TNM-L

## Application News

**No.** SCA-130-105

Sum parameter – Total Organic Carbon

### TOC determination in solid samples using the suspension method

The TOC content in solids plays an important role in the classification of soils, sludges and sediments. According to the German Ordinance on Environmentally Compatible Storage of Waste from Human Settlements (Abfallablagungsverordnung, AbfAbIV), TOC in solid materials is one of the key parameters for the characterization of wastes as part of the acceptance control of landfills. This important control measure requires a fast and simple TOC determination method and, at the same time, a robust and statistically reliable method that is based on the inhomogeneous composition of soils.



To date, the established regulations describe a method whereby a weighed solid sample is combusted in a stream of air or oxygen. The CO<sub>2</sub> generated during combustion is subsequently detected and quantified using a calibration curve. The inhomogeneity of the soils has a direct effect on the distribution of the measuring data – each weighed solid sample can only be combusted once.

#### ■ Suspension method

Several years ago, Shimadzu developed the so-called suspension method in cooperation with responsible authorities and the Albo-tec environmental laboratory in Bochum, Germany. In this method, the solid sample is processed in a specific way so that it can subsequently be treated as a liquid, particle-containing sample. This method was successfully applied in several round robin tests and has, since June 2009, also been described in the draft DIN EN 159536. This new standard is intended to replace DIN EN 13137 and describes the established solid sample combustion method as well as the novel suspension method (see annex).

#### ■ Analytical process



Approximately 200 mg of the dried and ground sample is weighed into an Erlenmeyer flask. The sample is subsequently suspended in a diluted hydrochloric acid solution. The acidic solution serves to break down the carbonates present in the sample and, at the same time, form the suspension medium.

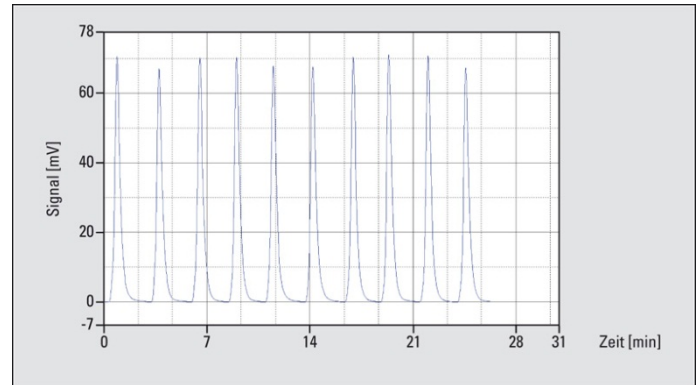


The suspension is homogenized for several minutes at a speed of 17,000 – 18,000 rpm using a dispersion unit. It is critically important to select a suitable precision tool. After homogenization, the suspension is transferred directly to autosampler vials. Critical for subsequent measurement is the use of a magnetic stirrer in the autosampler to ensure that the suspension remains homogeneous during sampling. After all, the small particles should not sediment, but remain uniformly distributed throughout the solution. The suspensions can now be repeatedly injected and analyzed.



This method enables not only automated solid sample analysis using an autosampler, but also parallel measurement of solid and liquid samples in the same sample table and the same sample tray. In addition to speed, this method is also impressive in terms of robustness. The possibility of multiple injections enables differentiation of small variations due to weighing and measuring.

### ■ Example of suspension determination



NPOC-Method (Acidification is done by creation of the suspension)

Sparge-time: 5 Minutes

Injection volume: 90µl

Multi-Injection is deactivated

### ■ Statistic

Peak-No	Areas	Result of suspension TOC in mg/l	Result of Sample TOC in %
1	183,7	24,71	2,47
2	180,9	24,23	2,42
3	189,0	25,61	2,56
4	183,8	24,72	2,47
5	179,9	24,06	2,41
6	179,9	24,06	2,41
7	179,9	23,89	2,39
8	186,9	25,25	2,53
9	181,6	24,35	2,37
10	177,6	23,67	2,37
<b>MW</b>	<b>182,2</b>	<b>24,5</b>	<b>2,45</b>
<b>RSD in%</b>	<b>1,88</b>	<b>2,52</b>	<b>2,49</b>

### ■ Recommended analyzer / Configuration

TOC-L<sub>CPN</sub>

ASI-L (40ml) with stirrer option and external Sparge-Kit.

## Application News

**No.** SCA-130-106

Sum parameter – Total Organic Carbon

### TOC determination in particle-containing samples - Cellulose test according to EN 1484

Depending on their origin, different effluents can contain substantial amounts of insoluble solids. These include clearly visible components that, in some cases, sediment very quickly. This applies particularly to heavy particles such as sand grains. Suspended solids such as fibers or flakes are naturally less likely to sediment. However, they also cause a certain inhomogeneity of the sample matrix.



A variant of TOC determination is the detection of DOC, Dissolved Organic Carbon. The wastewater sample is filtered through a membrane filter with a 0.45 µm pore size and subsequently measured. In contrast to DOC, TOC (Total Organic Carbon) determinations must detect the total organic carbon in a sample, including the insoluble components.

According to DIN 1484, the suitability of a TOC measurement system for the analysis of wastewater samples that contain solid matter must be tested. This is carried out using the so-called cellulose test (Appendix C of the above-mentioned standard).

#### ■ Cellulose test according to DIN EN 1484

The cellulose test is based on an aqueous cellulose suspension with a carbon content of 100 mg/L. This corresponds to 225 mg cellulose. The particle size ranges from 20 µm to 100 µm. Homogenization may only be carried out under stirring. Alternative methods such as ultrasound can break up the particles and thereby provide erroneous results. Large particles in particular have a tendency to sediment rapidly.

Stirring speed is critical for this reason. Very slow stirring leads to increased particle sedimentation. Extremely high stirring speeds lead to inhomogeneous particle distribution due to centrifugal force. DIN 38402 part 30, dealing with sample homogenization, serves in this context as an excellent reference. A solution should be stirred in such a way that the vortex will amount to 10% of the filling level.

For three consecutive injections, the mean value must lie within the range of 90 mg C/L to 110 mg C/L (corresponding to a recovery of 90 – 110 %). The relative standard deviation (RSD) may not exceed 10 %.

### ■ Particle tolerance of the TOC-L series

This test was carried out using a TOC-L system (TOC-L<sub>CPH</sub> including ASI autosampler with integrated stirring option).



### ■ System Configuration

- TOC-L CPX
- ASI-L (40ml recommended) with particle needle I
- Stirrer option
- Offline-Port can be used too

The TOC-L<sub>CPH</sub> was first calibrated using the automated dilution function in the range of 10 – 100 mg/L.

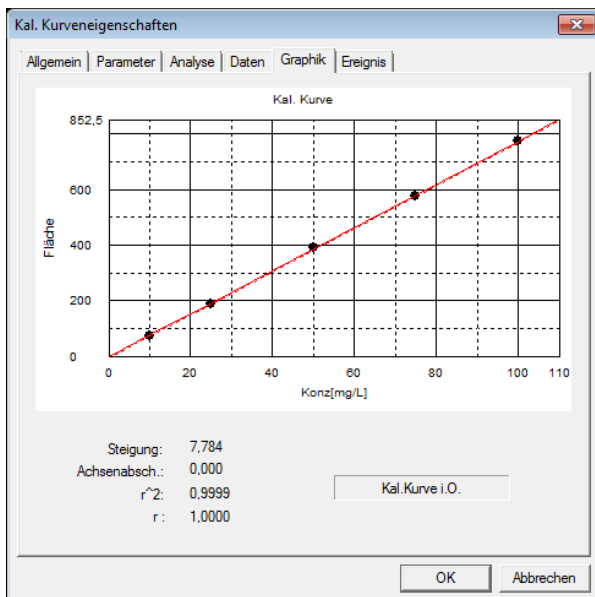


Figure 1 Calibration curve 10-100mg/L

### ■ Settings

- Injection volume 90  $\mu$ L
- TC measurement for the particle test
- NPOC measurement in the autosampler
- Stirrer in the ASI-L,
- medium stirring speed
- No multiple injection

### Used Cellulose-Standard:

Cellulose powder MN 100  
Particle size: 20-100 $\mu$ m  
Supplier: Machery-Nagel

### ■ Results

The cellulose suspension was injected five times according to the above settings.

NPOC = 98,4  $\pm$  2,2 mg/l (RSD = 2,27 %).  
This corresponds to a recovery of 98,4 %.

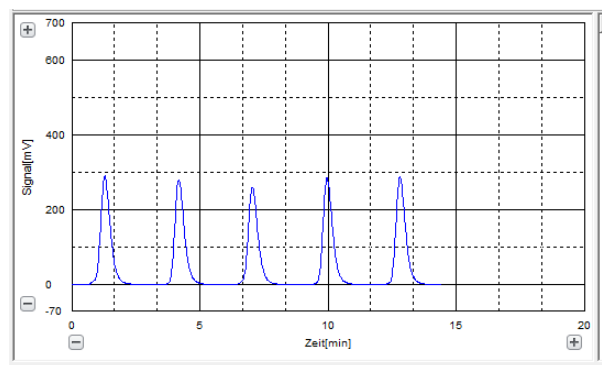


Abb.2 Peak graph of cellulose-suspension

These values are clearly within EN DIN specifications



## Application News

**No.** SCA-130-107

Sum parameter – Total Organic Carbon

Determination of particulate organic  
carbon after filtration  
(glass fiber suspension)

A limnological research laboratory tackled the problem of determining the particulate TOC content of the sample independently of DOC (Dissolved Organic Carbon) content. The water sample was filtered through filters of varying pore sizes. Particles of varying sizes remain on the filter. The question arose, how particulate TOC can be best measured.



Fig. Used glass fiber filter

A possibility would be to shred the filter and disperse it in water, and to measure the obtained suspension directly using the TOC system. This requires use of TOC-free glass fiber filters. This uncommon question requires a field test. Based on the melting range of glass fiber (about 550 °C) it was necessary to ensure that the glass fiber content would not clog or deactivate the catalyst (680 °C) and to establish where the oxidizing power diminishes.

### ■ The field test

A TOC analyzer with autosampler was used for the field test. After calibration of the TOC system, the test solution was measured 10 times. The test solution consisted of a glass fiber suspension in hydrochloric acid (five glass fiber filters dispersed in 500 mL) that was continuously stirred during measurement. To test the catalyst, a standard solution with a TOC of 50 mg/L was injected after each 10<sup>th</sup> measurement. After 100 injections and visual inspection of the catalyst and the catalyst tube, the measuring cycle was somewhat increased. Function of the catalyst was now checked using the standard test solution only after every 20 injections of the glass fiber suspension.



After a total of 450 injections, no visible change of the catalyst could be detected. Nor did the oxidative properties change or deteriorate in any way. Reproducibility of the results also did not reveal any change.

### ■ Statistics

As an example, the figure below shows the final 20 injections of the field test. Relative standard deviation was 1.8%.

The standard solution after the last glass fiber suspension injection cycle resulted in a TOC recovery of 97.6%.

The TOC field test clearly showed that the oxidative power of the catalyst, even after several hundred glass fiber suspension injections, did not deteriorate. Active centers of the catalyst were not affected, nor did they fuse.

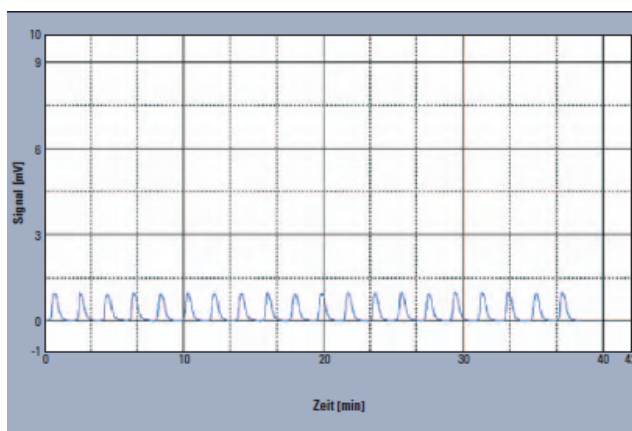


Fig. Peak graphs of the last 20 injections

Injection	Conc. In mg/l
1	0,7430
2	0,6947
3	0,6819
4	0,6850
5	0,6959
6	0,6930
7	0,6966
8	0,6831
9	0,6901
10	0,6997
11	0,6943
12	0,6890
13	0,6896
14	0,6871
15	0,6945
16	0,6934
17	0,6982
18	0,6936
19	0,6951
20	0,6924
<b>Mean Value</b>	<b>0,6945</b>
<b>SD</b>	<b>0,0124</b>
<b>RSD in %</b>	<b>1,78</b>

Tab. Peak areas and statistics of the last 20 injections

### ■ Recommended analyzer / Configuration

TOC-L<sub>CPN</sub>  
ASI-L (40ml) with stirrer option and external Sparge-Kit.



## 2. Pharmaceutical industry

Pharmaceutics is an ancient science that has supported people with remedies to help alleviate pain and heal illnesses. After medication, certain substances are expected to unfold their beneficial effects – while side effects from interfering substances and contaminations are undesirable. This is why it is important to use the purest possible substances and purified equipment and materials in the production of drugs.

To meet this standard, legislators have published Pharmacopoeias. These include methods and rules for the manufacture, storage, quality and testing of drugs. For drug manufacturers, complying with the rules and methods of the Pharmacopoeia is mandatory.

TOC determination is also described in the Pharmacopoeia (for instance the

European Pharmacopoeia = EP). The sum parameter serves as a measure of contamination by organic compounds. Not only the method itself is described, but also a test to verify the suitability of a TOC analyzer for the analysis.

In addition to ultrapure water required for the manufacture of drugs, water for injections – water that is directly injected into the bloodstream of the human or animal body – is also tested for its TOC content. The Pharmacopoeia actually specifies a maximum TOC limit value for such specific waters.

Many drugs are manufactured in batch mode operation. Prior to the production of the next batch, materials and working equipment must be extensively cleaned. In order to verify that the equipment is free from the 'previous'

drug batch, the TOC parameter is used for the evaluation of the cleaning process. The TOC not only mirrors the presence of drugs, but also reveals other contaminants such as those from cleaning agents.

With its TOC analyzers, Shimadzu offers systems that are suitable for many different TOC analysis issues in the pharmaceutical industry. In addition to the lowest detection sensitivity, the robust analyzers offer the highest precision and accuracy. Just like the analyzers themselves, the operation and evaluation software complies with all requirements of the FDA and the Pharmacopoeia.

Further information can be found in the individual application notes (for instance 'TOC determination in ultrapure water, cleaning validation or in accor-

dance with EP 2.2.44'). In addition to pharmaceutical applications, there are also application notes and information on 'Environmental analysis', 'Chemical industry', 'TOC special applications', 'TOC in daily practice' and 'TOC process analysis.'



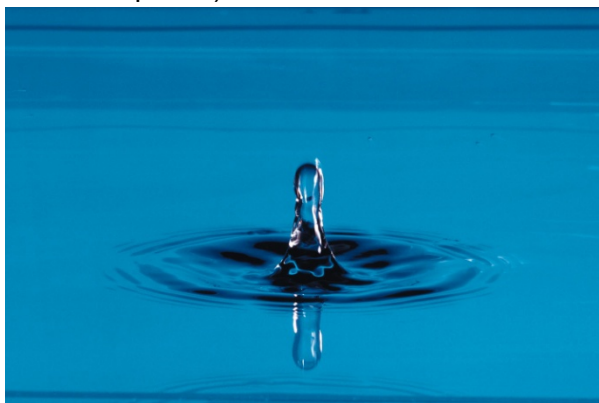
## Application News

**No.** SCA-130-201

Sum parameter – Total Organic Carbon

### TOC determination in ultrapure water – Comparison of the various oxidation techniques

Ultrapure water is one of the most widely used excipients in the production of pharmaceuticals. It is also used for cleaning purposes. Different application areas require different grades of ultrapure water quality. These grades are defined in the European Pharmacopoeia, which distinguishes between 'Purified Water', 'Highly Purified Water' and 'Water for Injection' ('The United States Pharmacopoeia, however, does not use the same classification as the European Pharmacopoeia').



**Water for injection** is used for the preparation of injection solutions and is produced by distillation. The TOC content may not exceed 0.5 mg/L (water for injection in bulk).

**Water Highly Purified** is a sterile ultrapure water for the manufacture of pharmaceuticals that do not require a 'Water for Injection' standard. It is also often used for the final rinse during cleaning and is usually produced by reversed osmosis. The TOC content may not exceed 0.5 mg/L.

**Water Purified** is used in the manufacture of pharmaceuticals that do not require any other standard. The organic content is determined either via the TOC value (0.5 mg/L) or via the permanganate test (purified water in bulk).

#### ■ TOC determination in ultrapure water

Two oxidation techniques are now commonly used in TOC analysis:

1. 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.
2. Wet chemical oxidation, which uses a combination of UV irradiation and persulfate for oxidation. Both methods can be applied for the determination of ultrapure water.



#### ■ TOC-L<sub>CPH</sub>: Oxidation via catalytic combustion

The TOC-L<sub>CPH</sub> uses the proven catalytic oxidation at 680 °C.

The integrated ISP sample preparation unit (an 8-position switching valve with syringe and sparging gas connection) considerably reduces the users' workload, as the instrument carries out dilution, acidification and sparging fully automatically.

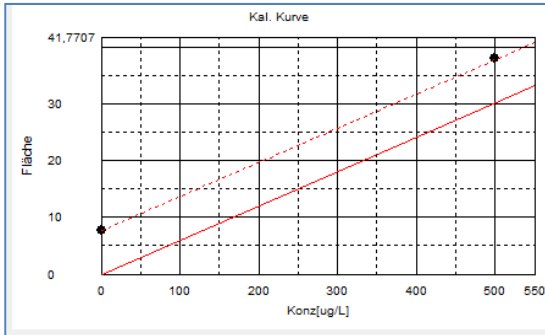


Fig. NPOC- Calibration (Blank and 500µg/L)

When using the high sensitivity catalyst, the detection limit is approximately 4µg/L. In addition, the combustion technique can be used in combination with the TNM-L module, whereby a single injection is sufficient for simultaneous determination of the total bound nitrogen. Simultaneous TOC/TN<sub>b</sub> determination is highly suitable for cleaning validation, as this enables differential determination between cleaning agent and product.

#### ■ TOC-V<sub>WP/WS</sub>: Wet chemical oxidation

The key technique of the TOC-V<sub>WP/WS</sub> analyzer is the powerful oxidation via the combination of sodium persulfate and UV oxidation at 80 °C. The TOC-V<sub>WP/WS</sub> features an automatic reagent preparation function that eliminates possible contamination of the persulfate solution. This ensures that the TOC value truly originates from the sample – and not from the reagent solution used. The large injection volume (up to 20.4 mL) in combination with the highly sensitive NDIR detector, leads to an extremely low

detection limit (0.5µg/L) and excellent reproducibility in the lower ppb range. The TOC-V<sub>WP/WS</sub> is therefore highly suitable for TOC determination in the ultra-trace range.

#### TOC-V WP Sample measurement

Method: NPOC (3% Acid, 3 min sparge)

Persulfatsol.: 1,5mL

Injection vol.: 20,4 mL

Result: 2,44 ± 0,42 µg/L TOC (NPOC)

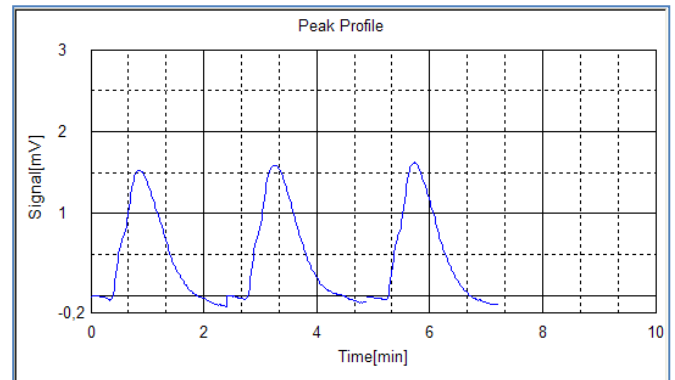


Abb. Peak graphik of TOC-V<sub>WP</sub> measurement

#### ■ Conclusions

Both types of instruments with their different oxidation methods can be used for TOC determination according to the European Pharmacopoeia. The advantage of the combustion method is its high oxidation potential, particularly for samples containing particulate matter. Moreover, simultaneous TOC/TN<sub>b</sub> measurements can be carried out, leading to a higher information content of the analysis. The advantage of wet-chemical oxidation is its high injection volume, which leads to higher sensitivity and therefore enables high precision measurements in the lower ppb range.

#### ■ Recommended analyzer / Configuration

TOC-L<sub>CPH</sub> with high sensitivity catalyst  
ASI-L (40ml), External Sparge-Kit.

TOC-V<sub>WP</sub> with ASI-V (40ml)

## Application News

**No.** SCA-130-202

Sum parameter – Total Organic Carbon

### TOC determination in cleaning validation – final rinse

The highest purity and most careful handling of substances and active ingredients is an important requirement in the manufacture of pharmaceuticals. An effective removal of production residues in pharmaceutical plants is an essential precondition. A well-cleaned pharmaceutical production system prevents contamination and, consequently, the adulteration of the produced drug. This is particularly important in the production of active ingredients in batch processes, as the system is used for different products and contamination of the next product must be prevented.



#### ■ Cleaning methods: Clean in Place

CIP cleaning (clean in place) is performed automatically and without disassembly of the production system. The production system must, therefore, have a CIP design. This includes the use of rinsing heads, no dead volumes, collection tank and recycling possibilities for the detergents.

Because time and temperature, as well as the use of cleaning agents and solvents are optimized, CIP cleaning is highly effective. Moreover, automatic cleaning allows a standardized and, therefore, an easily validated procedure.

#### ■ Sampling and analysis

In case of CIP cleaning, the rinsing liquid of the final rinse solution is sampled and analyzed. This is a very simple, easily automatable and fast method. When water is used as a solvent, TOC analysis is suitable for subsequent analysis.

#### ■ TOC-Analysis

TOC analysis is applied for the determination of the total organic carbon content as a sum parameter. The carbon content of the sample is oxidized to CO<sub>2</sub> and detected by an NDIR detector. Analysis of final rinse samples is, therefore, fast and simple (analysis time: approx. 4 min). The determined TOC value reflects any contamination by starting materials, products, byproducts or cleaning agents, as long as they contain carbon.

#### ■ Shimadzu TOC Series

With its TOC-L series, Shimadzu offers a highly suitable tool for cleaning validation. The modular design simplifies the analysis – no matter whether one wants to measure final rinse samples or swab samples.





The TOC-L<sub>CPH</sub> employs the proven catalytic oxidation at 680 °C. The integrated sample preparation (ISP) module greatly reduces the users' workload, as the instrument automatically carries out the dilution, acidification and degassing steps.

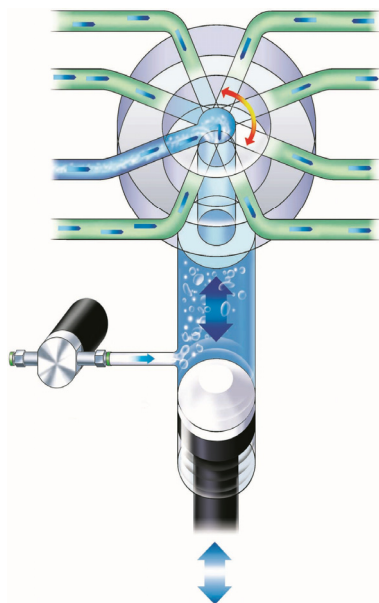


Fig. ISP-Module of TOC-L series

The possibility for simultaneous determination of the TNb (total nitrogen) using the TNM-L module enables, if necessary, a differentiation between cleaning agent and product. This may be of great importance, particularly for biopharmaceutical products.

For users who prefer wet-chemical oxidation for the determination of TOC, the TOC-V<sub>WP</sub> analyzer with its various options, is available. The key technique of the TOC-V<sub>WP</sub> analyzer is the powerful oxidation via the combination of sodium persulfate and UV oxidation at 80°C.

**Practical Example:**

■ **Instrument / Measurement parameter**

Unit: TOC-L<sub>CPH</sub>  
 Catalyst: High sensitivity catalyst  
 Meas.-typ: NPOC  
 Cal-Curve: 2-Punkt Calibration Curve  
 0-3 mgC/L (KHP)  
 Injection vol.: 500 µL

■ **Results**

Compound	TOC-Result	Recovery
Blank	0,030mg/L	
Tranexamic acid	2,14mg/L	105 %
Anhydrous caffeine	2,19mg/L	108 %
Isopropylantipyrine	2,20mg/L	109 %
Nifedipine	2,17mg/L	107 %
Gentashin ointment	0,117mg/L	4,35 %
Rinderon ointment	0,333mg/L	15,2 %

From the results, it can be concluded that the final rinse method only shows good recoveries for water-soluble compounds.

(Further information is available in the application note Japan TOC O41)

## Application News

**No.** SCA-130-203

Sum parameter – Total Organic Carbon

TOC –Determination in cleaning  
validation - swab method

Cleaning validation substantiates the effectiveness of a cleaning process and ensures that no residues remain on the surfaces of the production equipment. For the detection of contaminations, validated analytical methods must be used that are sensitive enough to determine the defined acceptable residue level. In general, residue limits of 10 ppm or 1/1000 of the usual therapeutic dose of an active substance are used as acceptance criteria.



### ■ Cleaning methods: Clean out of Place

For COP cleaning, the entire production system must be disassembled and the components must be cleaned individually. This procedure is very time consuming and labor intensive. Due to the individual cleaning, this procedure cannot be standardized. Advantages are, however, the low investment costs of the system and the possibility of visual inspection.

### ■ Sampling and analysis

In COP cleaning, the wiping method (swab) is used for sampling of visible residues. These include coatings, crusts, material deposited in corners and edges, and especially poorly soluble substances. The swab can be extracted in a solvent and the extracted solution is subsequently analyzed. If water is used for extraction, TOC analysis is suitable for subsequent analysis. Alternatively, the swab can also be measured directly (using a carbon-free swab) using a TOC solid-sample module.

### ■ Measuring system for the swab test

The modular design of Shimadzu's TOC-L series now enables the additional determination of the swabs using the same instrument. For this purpose, a solid-sample module (SSM-5000A) was connected to the main instrument, either a TOC-L series combustion system or the wet-chemical model of the TOC-V series.



For TC determination, the swab is placed in a ceramic boat and transferred into the oven, which is heated to 900 °C.

There, all carbon compounds are oxidized to CO<sub>2</sub>. To ensure complete oxidation, there is an additional catalyst in the combustion tube. The resulting CO<sub>2</sub> is then transported to the detector in the main instrument. The NDIR detector of the TOC-L series contains a tandem cell that consists of a long cell (200 mm) and a short cell (1 mm). By default, the long cell is used for water analysis and the short cell for solid-sample analysis. To attain a higher sensitivity for the analysis of solids, the solid-sample module can also be connected to the long, and thus the more sensitive, measuring cell. This can be realized using an upstream switching valve. This way, the system can now readily be used for cleaning validation without any loss in flexibility of switching between water and solid-sample analysis.

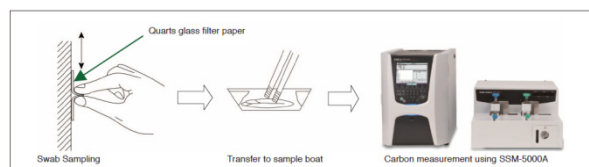
#### ■ Preparation

As the TOC analysis involves a sum parameter, it is important to ensure that the measured carbon really originates from the sampled surface. Some preparation is, therefore, important.

First, the swabs used must be carbon-free. This is why fiber optics swabs are used, which are annealed at 600 °C and are stored under dry conditions using an inert gas. The same pretreatment is required for the ceramic boat. All tools used, such as tweezers and glass containers must be free from carbon.

#### ■ Swab test

For the wiping test, two pretreated swabs are sampled, the lower swab is moistened with water and the defined surface is wiped according to the prescribed procedure. The used swab is now folded, placed in the clean ceramic boat and transferred to the TOC measuring system.



Depending on the expected concentration or defined limit value, the system configuration and calibration curve is selected. The calculated amount of carbon is now correlates directly to the area of the wiped surface.

#### ■ Practical example:

##### ■ Instrument/ Measurement parameter

Unit: TOC-LCPH + SSM-5000A  
(shortcut of IC-flow line)

Detector cell: Short Cell

Carrier gas: 400 mL/min oxygen (SSM)

Meas.-typ: TC

Cal-Curve: 1-Point Calibration curve with 30µL of 1%C Glucose solution

Swab: Advantec QR-100 quartz glass Filter paper (45 mm)  
Prepared at 600°C, 15min

#### ■ Result

Compound	TOC-Result	Recovery
Blank	0,00	
Tranexamic acid	202 µgC	101 %
Anhydrous caffeine	201 µgC	100 %
Isopropylantipyrine	210 µgC	105 %
Nifedipine	212 µgC	106 %
Gentashin ointment	200 µgC	100 %
Rinderon ointment	209 µgC	104 %

(Further information is available in the application note Japan TOC O41)



## Application News

Sum parameter – Total Organic Carbon

TOC-Determination according to EP 2.2.44

**No.** SCA-130-204

Since the USP (United States Pharmacopoeia) regulations for the determination of Aqua Purificata and Aqua ad injectabilia has been implemented into the European Pharmacopoeia (EP), TOC analysis has become increasingly established in quality control. Users who test the TOC content in pharmaceutical water must regularly test their TOC system using a system suitability test according to the method described in the EP 2.2.44 guidelines.



### ■ European Pharmacopoeia

The EP 2.2.44 guidelines do not prescribe any particular oxidation technique for TOC determination. The TOC systems, however, must be able to differentiate between inorganic and organic carbon. This can be carried out either via removal of the inorganic carbon (NPOC method), or via a separate determination (difference method). The limit of detection for TOC should be at least 0.05 mg /L. The applicability of the method must be determined via a system suitability test.

### ■ System suitability test

For the system suitability test, a standard sucrose solution with a carbon content of 0.5 mg/L is prepared. A control solution of 1,4-benzoquinone with the same carbon content was subsequently prepared. The blank water (ultra-pure water) used for this purpose may not exceed a TOC content of 0.1 mg/L. For the system suitability test, all solutions including the blank water are subsequently measured and the resulting signals are recorded.

Blank water:  $r_w$

Standard solution (sucrose):  $r_s$

Control solution (benzoquinone):  $r_{ss}$

The peak area of the blank water is subtracted from the peak areas of both standard solutions. The recovery of the benzoquinone standard is then calculated with respect to the sucrose standard.

$$\text{Recovery in \%: } \frac{r_{ss} - r_w}{r_s - r_w} \times 100$$

Results between 85 - 115% are acceptable. The ultrapure water sample corresponds to the guidelines when its response signal ( $r_u$ ) does not exceed  $r_s - r_w$ .



**■ TOC-Control L software**

The TOC-Control L software simplifies the implementation of the system suitability tests using integrated templates for the creation of calibration curves and the measurement of the control sample.

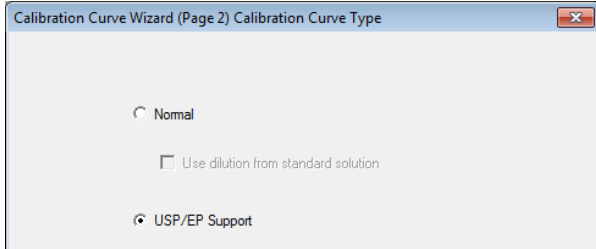


Fig. Calibration curve wizard

The following figure shows an example of an EP calibration curve (2 points, blank and 500 µg/L).

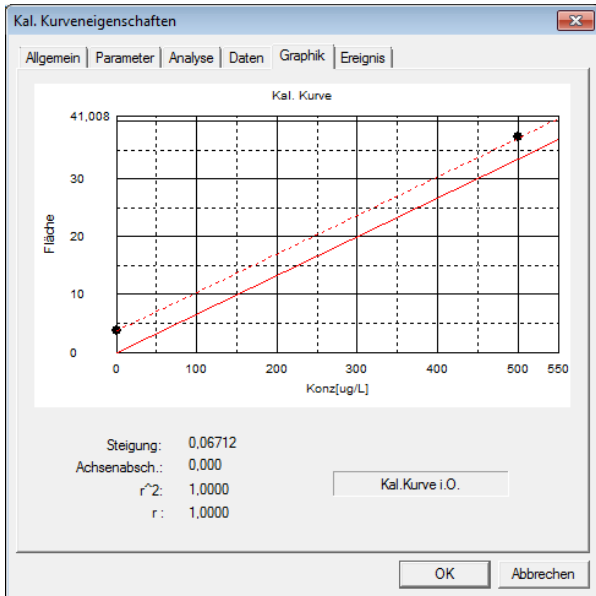


Fig. Calibration Curve

The determination of benzoquinone is set in the sample / method properties wizard.

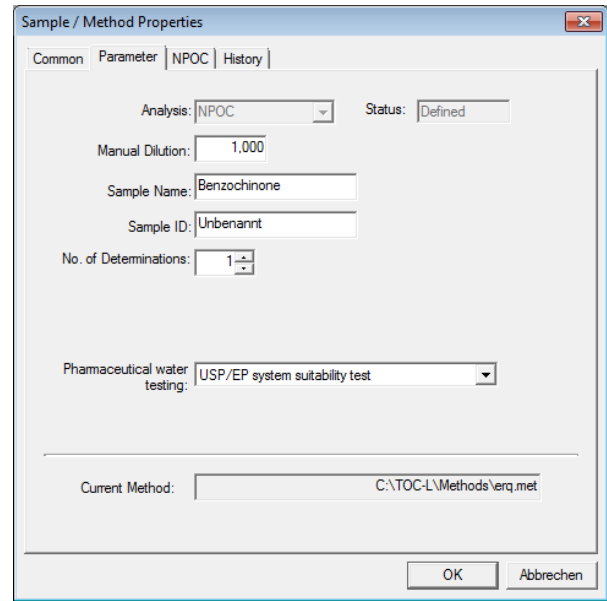


Fig. Benzochinone-Determination

After measuring the benzoquinone sample, the software automatically calculates the recovery according to EP 2.2.44, whereby the peak area values for the blank sample and the sucrose sample are obtained from the calibration curve. The result is listed under the column 'Notes' in the sample table (Figure below).

Washing / Untitled NPOC:0,000mg/L						
	Typ	Analyse	Probenname	Original	Ergebnis	Notizen
15	Unbekannt	NPOC	Washing		NPOC:0,000mg/L	
16	Unbekannt	NPOC	Washing		NPOC:0,000mg/L	
17	Standard	NPOC	Untitled	npoc_sucrose_500ppb.2012_02_03_13_37_01.cal		
18	Unbekannt	NPOC	Benzochinon	npoc_sucrose_500ppb.cal	NPOC:592,7ug/L	107.5% : USP/EP system suitability test: Pass
19	Unbekannt	NPOC	Washing		NPOC:0,000mg/L	

Fig. Result of system suitability test in sample table



### 3. Chemical industry

The most commonly used compound in the chemical industry is water – not only as a solvent in processing, but also as an energy carrier in the cooling or heating cycle. As vast amounts of water are needed, chemical industries are often located close to large bodies of flowing water. Water used as processing water or as cooling water is cleaned and subsequently led back to the river or stream. For environmental protection, these waters are subject to specific control and monitoring measures. As the TOC non-specifically detects all organic compounds, this parameter has also proven to be invaluable here.

Large chemical industrial parks have their own wastewater treatment plants for cleaning wastewaters emanating from the various chemical plants. In order to evenly distribute the wastewater charges over the participating

companies, the TOC load of the individual wastewaters is often used as a basis for calculation. Companies delivering higher TOC loads are required to pay higher charges.

Incoming goods control is important in the chemical industry. Impurities present in reagents often also constitute the impurities in products. In addition to the targeted analysis of known compounds, sum parameters can help to assess the raw chemicals in terms of their impurities. The TOC plays an important role here: this parameter describes the contamination through organic compounds and specifies the total amount of organic carbon. TOC can, therefore, also be used for the assessment of inorganic chemicals.

The great challenge for TOC measurements in chemical products is to devel-

op protective mechanisms to help protect instruments and their components, as well as to prevent damage by, for instance, acid fumes or high salt loads. For this purpose, Shimadzu's TOC-L series offers several gas washers and options to ensure safe and problem-free analyses.

A further challenge is to attain a stable and reproducible oxidation to ensure that no fluctuating or strongly tailing peaks are recorded. In addition, the measuring values should remain stable over a longer measuring interval.

In order to cover this wide range of analytical tasks in the chemical industry, flexible systems are needed that are easily adapted to the task in question via various options, kits and modules. Shimadzu offers TOC systems that are highly suitable for such analytical prob-

lems. Because of their modular design, the instruments in the TOC-L series can be equipped for any possible measurement task.

The individual application notes (for instance 'TOC determination in hydrochloric acid, brines or sodium hydroxide') contain further information. In addition to applications in the chemical industry, application notes are also available on 'Pharmaceutical industry', 'Environmental analysis', 'TOC special applications', 'TOC in daily practice' and 'TOC process analysis.'



## Application News

Sum parameter – Total Organic Carbon

### TOC – Determination in hydrochloric acid

**No.** SCA-130-301

Acids, in particular concentrated hydrochloric acid, represent a large group of inorganic chemicals frequently used in the chemical industry. TOC determination in concentrated hydrochloric acid poses an enormous challenge to the analyzers that are used for this purpose.

In general, it is possible to greatly dilute the substance to be analyzed in order to eliminate matrix interferences. But sometimes it is necessary to achieve very low limits of detection (with reference to 37% hydrochloric acid) of 1 mg/L.



TOC-L CPH with OCT-L

#### ■ Acid challenge

The great challenge is to develop protective mechanisms to help protect instruments and their components, as well as to prevent damage by acidic fumes. For this purpose, the TOC-L series offers several gas washers that bind and eliminate the chlorine gas formed in the flow line of the system in various ways.

Another challenge is to attain a stable and reproducible oxidation process to ensure that no fluctuating or tailing peaks are being recorded. In addition, the measuring values should remain stable over a longer measuring interval.

#### ■ TOC Measuring Method

The 37% hydrochloric acid solution was manually diluted to a ratio of 1:2 with water in order to obtain an 18.5% hydrochloric acid solution.

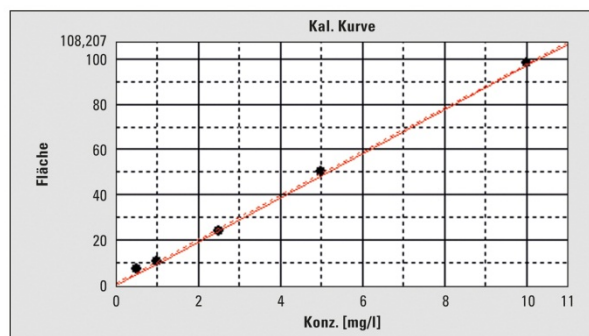


Abb.2 Mehrpunktkalibration mit Verdünnungsfunktion

Calibration was carried out in the range of 0.5 to 10 ppm. The automatic dilution function of the analyzer automatically executes this calibration from a single stock solution. The injection volume was 150 µL. In case the TOC contamination of the hydrochloric acid exceeds the measuring range of the calibration, the automatic dilution function of the analyzer will readjust the hydrochloric acid solution to fit the measuring range.

#### ■ Verification the measuring method

After calibration, the TOC content of the concentrated hydrochloric acid solution was determined.



To investigate matrix influences, a potassium hydrogen phthalate solution was subsequently added to the 18.5% hydrochloric acid solution to increase the TOC by 5 ppm (Figure 3 and Table 1).

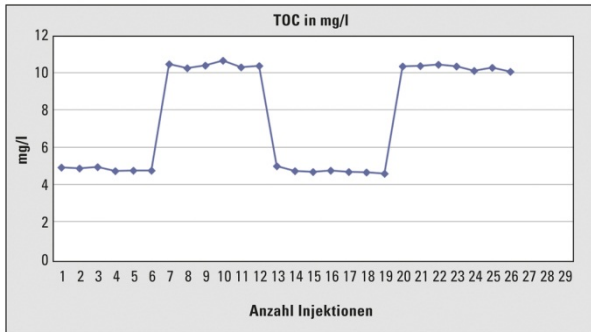


Fig.3: Results of original and spiked hydrochloric solution

Figure 3 and Table 1 show the results of the individual measurements of the hydrochloric acid as well as the measurements of the spiked hydrochloric acid.

TOC result of 18,5% hydrochloric acid in mg/l		
Injection	Original	Spiked with 5ppm TOC
1	4,901	10,46
2	4,858	10,24
3	4,91	10,39
4	4,716	10,64
5	4,728	10,28
6	4,739	10,35
7	4,966	10,34
8	4,71	10,36
9	4,662	10,42
10	4,733	10,33
11	4,659	10,11
12	4,625	10,27
13	4,552	10,06
Mean value	4,75	10,33
SD	0,12	0,15
RSD in %	2,6	1,4

Tab. 1: Values of each injection

### ■ Long-term stability

To investigate the long-term stability of the method, the 37% hydrochloric acid solution was again diluted to a ratio of 1:2 with water and injected 76 times (150 µL).

The relative standard deviation over all measurements was 3.4%. The following graph shows the progression of the TOC values of the hydrochloric acid injections.

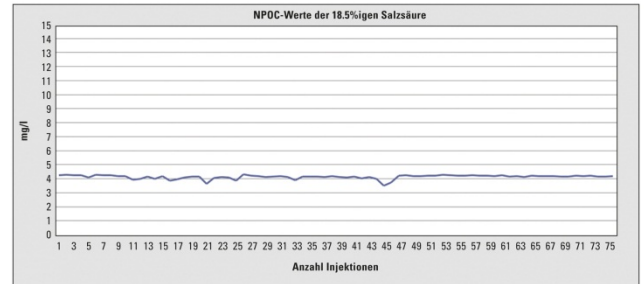


Fig.4: Result of longterm stability

Blank values and standards (10 ppm) were alternately measured between the individual measurements.

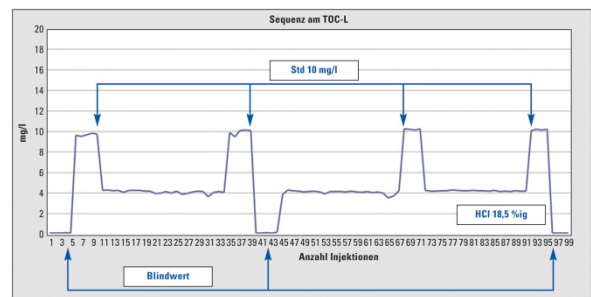


Fig. 5: Sequence of hydrochloric acid, blank (pure water) and Standards (10 mg/l)

### ■ Recommended analyzer / configuration

- TOC-L<sub>CPH</sub> with a normal sensitive catalyst (without glass wool at the bottom of the catalyst tube)
- B-Type scrubber with SnCl<sub>2</sub> solution
- Copper bead scrubber with pH paper
- Bypassing the blank check vessel
- Substituting water for phosphoric acid (IC vessel)
- OCT-L 8-port sampler

## Application News

Sum parameter – Total Organic Carbon

TOC – Determination in nitric acid

**No. SCA-130-302**

Organic contaminants present in basic chemicals may constitute the impurities in products. This is why quality control of the reactants is indispensable.



The determination of organic contaminations in concentrated nitric acid (69%) becomes a challenge when the required detection limit does not allow large dilution steps.

An example is the TOC determination in a 69% HNO<sub>3</sub> solution with a detection limit of < 10 mg/L.

### ■ Sample preparation

For sample preparation, the 69% HNO<sub>3</sub> solution was diluted to a ratio of 1:10 with ultrapure water.

Compound (concentration)	Dilution	Konz. [%]
Nitric Acid (69%)	1 : 10 diluted with water (5ml / 50ml)	Ca. 7%

Calibration of the TOC-L system was carried out using the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

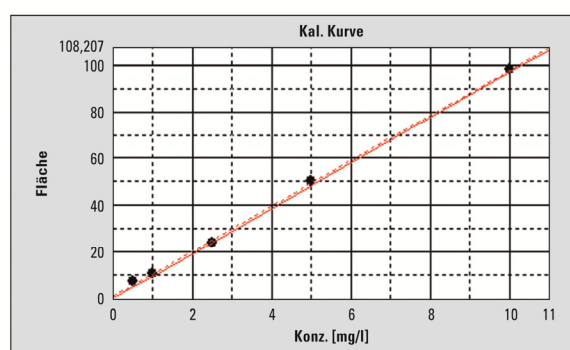


Fig. Multi-point calibration with dilution function

To protect the NDIR detector, the B-type scrubber was used together with the halogen scrubber.

### ■ Matrix interferences

In addition to CO<sub>2</sub>, various nitrogen oxides are formed from the organic components during the combustion of nitric acid. Excessively high levels of NO<sub>3</sub> can lead to significant amounts of N<sub>2</sub>O (nitrous oxide). Nitrous oxide exhibits absorption bands in the same IR detection range as CO<sub>2</sub> and can, therefore, be misinterpreted for CO<sub>2</sub>. In addition, nitrous oxide can cause tailing and can affect the peak symmetry.

Due to the high solubility of N<sub>2</sub>O in water, the gas is dissolved in the B-type scrubber and will not reach the detector.

### ■ Result

The duplicate NPOC determination of a nitric acid produced the following results:

Sample	NPOC [mg/l]	RSD [%]
Nitric Acid (69%)	36,9	1,4
Nitric Acid (69%)	33,4	3,0

To investigate this matrix influence, an additional dilution (1:10) of a 69% nitric acid solution was carried out and a potassium hydrogen phthalate stock solution was subsequently added to increase the NPOC content by 5 ppm. (Note: This corresponds to an increase to 50 ppm for the 1:10 dilution).

Sample	NPOC [mg/l]	RSD [%]
Nitric Acid (69%)	25,1	1,3
Nitric Acid (69%) Spiked with 50 ppm KHP	76,2	1,8

The use of suitable gas washers (scrubbers) enables reproducible TOC measurements in concentrated nitric acid.



### ■ Recommended Analyzer / Configuration

TOC-L<sub>CPH</sub> with normal sensitive Catalyst

B-Type-Scrubber

OCT-L (8-port Sampler)

## Application News

Sum parameter – Total Organic Carbon

### TOC – Determination in sulfuric acid

#### No. SCA-130-303

Acids are a group of frequently used inorganic chemicals used in the chemical industry. In particular, sulfuric acid is used in a wide range of applications.



Sulfuric acid in a concentration range to 1% can be directly measured using a TOC-L analyzer. Higher sulfuric acid concentrations can lead to tailing and, consequently to increased measurement values because high sulfate concentrations (> 5000 mg/L) can lead to the formation of large amounts of SO<sub>2</sub> vapors. SO<sub>2</sub> exhibits absorption bands in the same IR detection range as CO<sub>2</sub> and can, therefore, be misinterpreted for CO<sub>2</sub>.

To determine organic contaminations in highly concentrated sulfuric acid, additional SO<sub>2</sub> scrubbers are used.

The following SO<sub>2</sub> scrubbers are available:

- Sulfix (WAKO Chemicals, Fuggerstr. 12, 41468 Neuss, Germany). The Sulfix scrubber is installed underneath the normal sensitive catalyst and enables selective filtration of the formed SO<sub>2</sub>.
- Mist scrubber (cartridge)  
Just like the halogen scrubber, the 'Mist scrubber' is used in the flow line for SO<sub>2</sub> absorption.

In the experiment described below, the NPOC content of a 98% sulfuric acid solution is determined.

The required purity criterion and the required limit of detection was < 10 mg/L.

#### ■ Sample preparation

The concentrated sulfuric acid was diluted with ultrapure water to a ratio of 1:10 to decrease the concentration as well as the viscosity of the sulfuric acid.

Compound (Concentration)	Dilution	Conc.
Sulfuric acid (98%)	1 : 10 diluted with water (5m/50ml)	Ca. 10%

The dilution has to be carried out with the utmost care and caution, as the sulfuric acid reacts violently upon the addition of water (heat generation).



The system is calibrated using the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

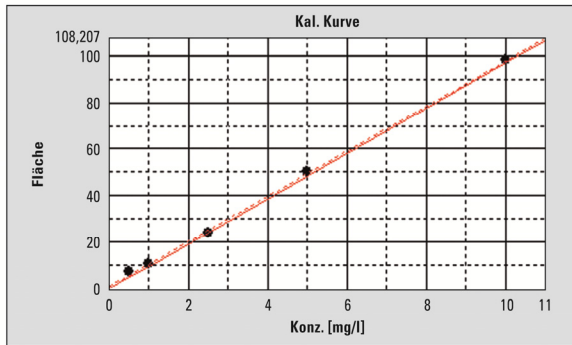


Fig. Multi-point calibration with dilution function

### ■ Kit for high-salt samples

For the determination, a TOC-L<sub>CPH</sub> equipped with a kit for high salt loads was used. The kit consists of a special catalyst tube, a special mixture of various catalyst beads and a ceramics grid, which replaces the platinum net.

Sample acidification when using the high-salt kit, is carried out with sulfuric acid. Sulfuric acid is used to modify the sample matrix. While NaCl has a melting point of 801 °C, the melting point of NaSO<sub>4</sub> is higher (881 °C). This has a positive effect on the lifetime of the combustion tube.

For this reason, sulfuric acid is measured directly using the high-salt kit.

### ■ Result

The duplicate determination of sulfuric acid yielded the following results:

Sample	NPOC [mg/l]	RSD [%]
Sulfuric acid (98%)	<10 (4,6)	-
Sulfuric acid (98%)	<10 (5,4)	-

The sulfuric acid fulfilled the required purity criteria of TOC < 10 mg/L.

The use of suitable gas washers (scrubbers) enables reproducible TOC measurements in concentrated sulfuric acid.



### ■ Recommended analyzer / Configuration

- TOC-L<sub>CPH</sub>
- OCT-L
- High-Salt-Kit
- B-Type-Scrubber with diluted hydrochloric acid with wire net.
- Mist-Scrubber

## Application News

Sum parameter – Total Organic Carbon

### TOC – Determination in brines

#### No. SCA-130-304

The determination in difficult matrices, such as brines or heavily contaminated wastewaters, presents a special challenge for TOC analyzers. In the chemical industry, brines with a salt load (NaCl) of up to 28% are used for chlor-alkali electrolysis. For this process it is important to know the TOC content.

The unique feature of this application does not inherently lie in the conversion of the carbon components to carbon dioxide, but in the salt load associated with the matrix. This leads to higher maintenance needs, as the salt can crystallize in the combustion system.

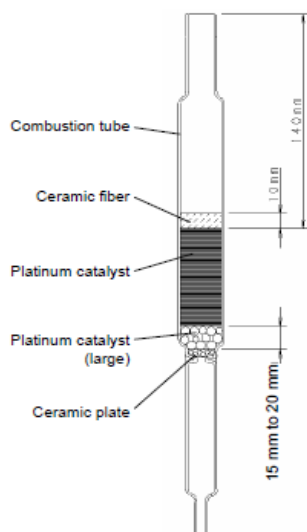
#### ■ Kit or high-salt samples

The TOC-L series features a kit for high-salt samples, which significantly increases the instrument's availability. The kit consists of a combustion tube of a special geometry and a unique catalyst mixture.

In this application, sample acidification is carried out with sulfuric acid. Sulfuric acid modifies the sample matrix. Whereas the melting point of NaCl is 801 °C, NaSO<sub>4</sub> has a higher melting point is (888 °C). The potassium salts of sulfuric acid also have a significantly higher melting point than those of hydrochloric acid. This extends the lifetime of the combustion tube.

Compound	Melting point
NaCl	801°C
KCl	773°C
Na <sub>2</sub> SO <sub>4</sub>	888°C
MgCl <sub>2</sub>	708°C
CaCl <sub>2</sub>	782°C
K <sub>2</sub> SO <sub>4</sub>	1.069°C

Tab. Melting point of different salts



#### ■ Sample preparation

The determination of organic contaminations in a pure brine (30% sodium chloride solution) is described below. For such highly concentrated salt solutions, the principle of diluting the sample as much as possible applies. As the required detection limit was at < 1 mg/L, the samples were diluted with ultrapure water to a ratio of 1:1. Dilution was carried out manually in a 50 mL volumetric flask under the addition of several drops of concentrated sulfuric acid (25%).

Compound (Concentration)	Dilution	Conc.
Brine solution (30%)	1 : 2 diluted with water (25ml/50ml) add. 1-2 drops Sulfuric acid until pH<7	ca. 15%ig

For the analysis a TOC-L<sub>CPH</sub> equipped with a kit for high salt loads was used. The system is calibrated using the automated dilution function in the range of 0.5 mg/L to 10 mg/L.

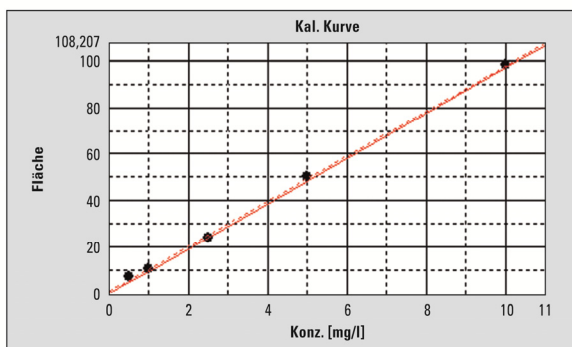


Fig. Multi-point calibration with dilution function

### Result

The duplicate determination of the TOC analysis yielded the following results:

Sample	NPOC [mg/l]	RSD [%]
Brine solution (30%)	3,6	1,8
Brine solution (30%)	3,6	1,8

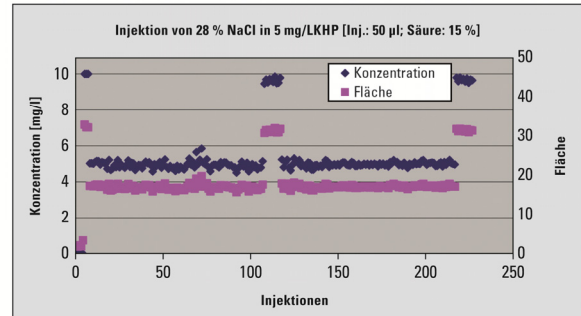
### Stability test

In this test, the long-term stability of the combustion system was tested. The system was calibrated to 10 mg/L with an injection volume of 50 µL.

A 28% NaCl solution was prepared and spiked with a KHP solution to obtain a 5 mg/L TOC solution and a 15% sulfuric acid solution was added.

Initially, a blank value and a control standard (10 mg/L) were measured, and the NaCl solution was subsequently injected.

The control standards were tested after 110 and 220 injections of the brine solution, respectively.



Maintenance of the combustion tube and the catalyst was not necessary after the measurements were completed. Only the TC-slider needed to be cleaned. The figure above shows the excellent reproducibility's and the stability of the measurement.



### Recommended Analyzer / Configuration

TOC-L<sub>CPH</sub>  
High-Salt-Kit  
B-Type-Scrubber

## Application News

**No. SCA-130-305**

Sum parameter – Total Organic Carbon

TOC – Determination in sodium hydroxide solution

Organic contaminants in basic chemicals may lead to impurities in the products. Therefore, quality control of the reactants is necessary.



The TOC determination in sodium hydroxide can lead to various problems. The catalyst and the combustion tube wear out very rapidly. This, in turn, will lower the sensitivity at an equally fast rate and leads to very poor reproducibilities.

NaOH can also absorb CO<sub>2</sub> from the environment. As air contains approximately 400 ppm CO<sub>2</sub>, direct TC determination in sodium hydroxide can lead to much higher values. The NPOC method is, therefore, recommended for the determination of organic contaminations in sodium hydroxide. The sample should also be diluted as much as possible.

In the present case, a 50% sodium hydroxide solution was analyzed. The purity criterion and the required limit of detection was < 10 mg/L.

### ■ Sample Preparation

The sample was first manually diluted to a ratio of 1:10 with ultrapure water and a suitable amount of acid.

Several mL of ultrapure water were placed in a 50 mL volumetric flask. Subsequently, 5 mL of the concentrated sodium hydroxide was pipetted into the flask. Finally, concentrated sulfuric acid was added until the solution has reached a pH < 2. The flask was then filled with ultrapure water up to the mark. The addition of sodium hydroxide, as well as the addition of sulfuric acid to the water must be done with the utmost care and caution, as a violent chemical reaction occurs.

Compound (Concentration)	Dilution	Conz. [%]
Sodium hydroxide solution (50%)	1 : 10 diluted (5 ml / 50 ml) add. 1-2 drops Sulfuric acid until pH<7 (Note: generation of heat)	approx. 5% + Sulfuric acid

Calibration of the TOC-L system was carried out using the automatic dilution function within the range of 0.5 mg/L to 10 mg/L.

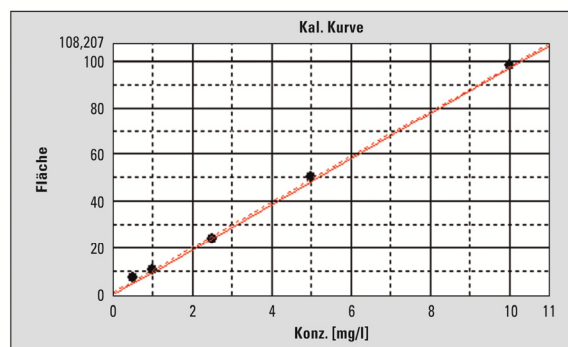
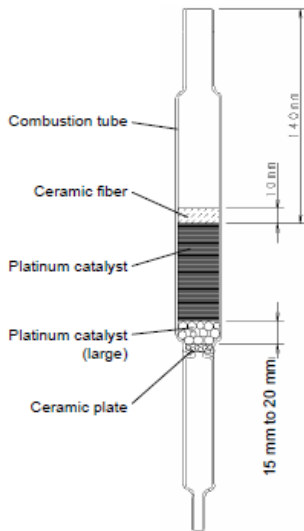


Fig. Multi-point calibration with dilution function



### ■ Kit for high salt samples

For the determination, a TOC-L<sub>CPH</sub> was equipped with a kit for high salt loads. The kit consists of a special catalyst tube, a special mixture of various catalyst beads and a ceramics grid, which replaces the platinum net.



When using the high-salt kit, sample acidification is carried out with sulfuric acid, which is used here to modify the sample matrix. Compared to NaCl with a melting point of 801 °C, the melting point of NaSO<sub>4</sub> is higher (881 °C) which extends the lifetime of the combustion tube.

### ■ Results

The 5% sodium hydroxide can now be measured using the NPOC method. The duplicate determination of the sodium hydroxide yielded the following results.

Sample	NPOC [mg/l]	RSD [%]
Sodium hydroxide (50%)	<10 (8,2)	-
Sodium hydroxide (50%)	<10 (8,3)	-

The sodium hydroxide met the required purity criteria of < 10 mg/L TOC.

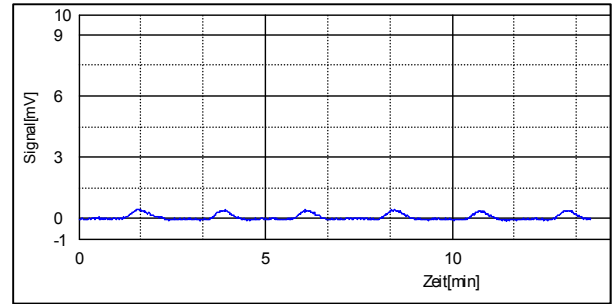


Fig. Example peaks of 50% sodium hydroxide solution



### ■ Recommended Analyzer / Configuration

TOC-L<sub>CPH</sub>  
OCT-L (8-port samples)  
High-Salt-Kit  
B-Type-Scrubber

## Application News

Sum parameter – Total Organic Carbon

### TOC – Determination in soda solution

**No.** SCA-130-306

Impurities in products can be caused by organic contaminants present in basic chemicals to. That is a reason why quality control of the reactants is indispensable.



In the determination of organic contaminations in concentrated soda solutions, various issues must be considered. In comparison to organic carbon, the soda solution to be investigated has a very high inorganic carbon content in the form of carbonates. In addition, the solution has a high pH value and tends to absorb carbon dioxide from the air.

A soda solution must, therefore, be analyzed using the NPOC method.

In the case described here, a 50% soda solution was investigated. The required detection limit was 10 mg/L.

#### ■ Sample preparation

The sample was first manually diluted to a ratio of 1:10 with ultrapure water and a corresponding amount of acid. Several mL of ultrapure water were placed in a 50 mL volumetric flask. Subsequently, 5 mL of the concentrated soda solution was pipetted into the flask. Finally, concentrated sulfuric acid was added until the solution has reached a pH < 2.

The flask was then filled with ultrapure water up to the mark.

Compound (Concentration)	Dilution	Conc.
Soda hydroxide solution (50%)	1 : 10 diluted with water (5ml/50ml) add. 1-2 drops Sulfuric acid until pH<7	Approx. 5%

**Caution:** During the addition of the sulfuric acid, the carbonates decompose under a violent reaction (heat dissipation / gas formation).

Calibration of the TOC-L system was carried out using the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

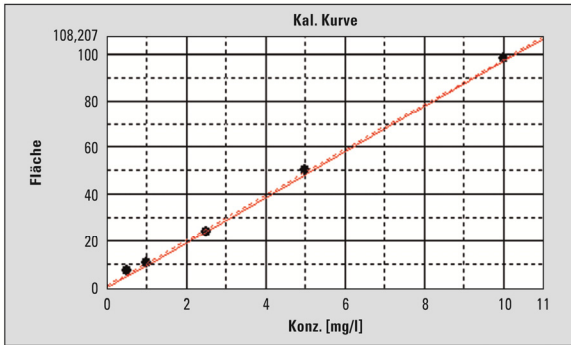
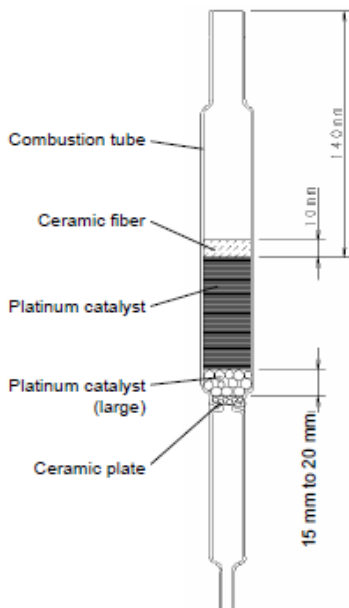


Fig. Multi-point calibration with dilution function

For the determination, a TOC-L<sub>CPH</sub> was equipped with a kit for high salt loads. A special catalyst tube, a special mixture of various catalyst beads and a ceramics grid, which replaces the platinum net are part of the kit.



Sample acidification when using the high-salt kit, is carried out with sulfuric acid in order to modify the sample matrix.

The higher melting point point of NaSO<sub>4</sub> (881 °C) compared to NaCl (801 °C) has a positive influence on the lifetime of the combustion tube.

### ■ Results

The duplicate determination of the soda solution yielded the following results:

Sample	NPOC [mg/l]	RSD [%]
Soda solution (50%)	56,4	7,1
Soda solution (50%)	54,8	4,9

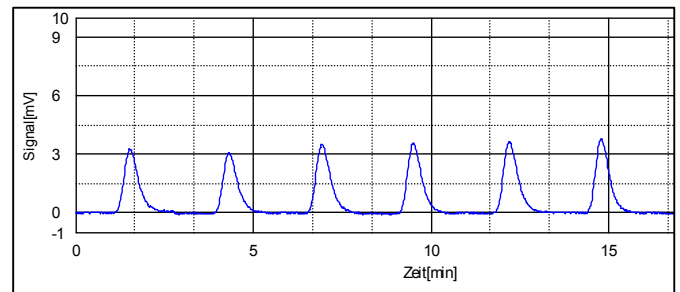


Fig. Peak graphs of a diluted soda solution (ca.5%)



### ■ Recommended Analyzer / Configuration

- TOC-L<sub>CPH</sub>
- ASI-L
- High-Salt-Kit
- B-Type- Scrubber

# Application News

Sum parameter – Total Organic Carbon

## TOC – Determination in ammonia or ammonium salt solutions

**No. SCA-130-307**

Basic chemicals may contain organic contaminants polluting end products. This is why quality control of the reactants is a must.

In the TOC determination of ammonia water or concentrated ammonium salt solutions, various issues must be considered. Ammonia and some ammonium salts are alkaline. The catalyst and combustion tube are sensitive to alkaline media and are subjected to increased wear.



The solutions should, therefore, be acidified and possibly be diluted.

The decomposition during oxidation of the ammonium or ammonia proceeds to completion without the formation of residues on the catalyst. Therefore, it is not necessary to use a high-salt kit.

In the case described below, the NPOC content of a 40% ammonium nitrate solution was determined. The required detection limit was < 10 mg/L.

### ■ Sample preparation

The ammonium nitrate solution was diluted with ultrapure water to a ratio of 1:10. Dilution was carried out manually in a 50 mL volumetric flask under addition of several drops of concentrated sulfuric acid (25%).

Compound (Concentration)	Dilution	Conc.
Ammonium nitrate solution (40%)	1 : 10 diluted (5 ml / 50 ml) add. 1-2 drops Sulfuric acid until pH<7 (Note: generation of heat)	Approx. 4%

Calibration of the TOC-L system was executed using the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

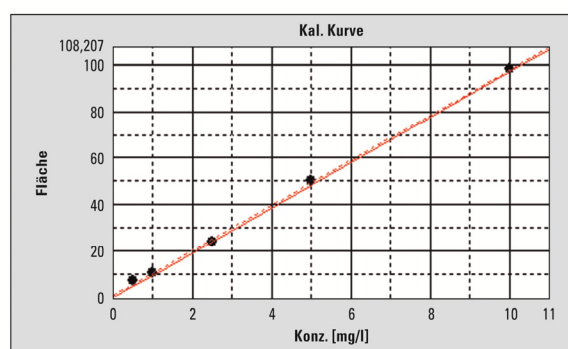


Fig. Multi-point calibration with dilution function



### ■ Interferences

In addition to CO<sub>2</sub> formed from the organic components, various nitrogen oxides are formed during the combustion of ammonium salts or ammonia water. Excessively high nitrogen levels can lead to the formation of significant amounts of N<sub>2</sub>O (nitrous oxide). Nitrous oxide exhibits absorption bands in the same IR detection range as CO<sub>2</sub> and can, therefore, be misinterpreted for CO<sub>2</sub>. In addition, nitrous oxide can cause tailing and can affect the peak symmetry.

A B-type scrubber is used to eliminate possible interference by nitrous oxide. Due to the high solubility of N<sub>2</sub>O in water, the gas is dissolved in the B-type scrubber and will not reach the detector.

### ■ Results

The duplicate determination of the ammonium nitrate solution yielded the following results:

Probe	NPOC [mg/l]	RSD [%]
Ammonium nitrate solution (40%)	56,5	0,8
Ammonium nitrate solution (40%)	56,7	1,2

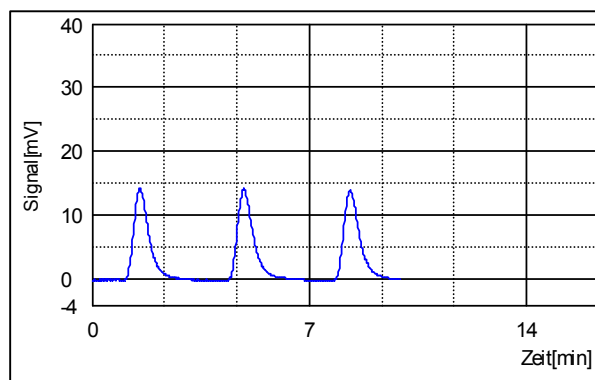


Fig. Example peaks of 40% ammonium nitrate solution



### ■ Recommended analyzer / Configuration

- TOC-L CPH
- OCT-L (8-port sampler)
- B-Type- Scrubber

## Application News

**No.** SCA-130-308

Sum parameter – Total Organic Carbon

### TOC – Determination in sodium nitrate and sodium nitrite

Basic chemicals may contain organic contaminants influencing the quality of products. Quality control procedures of the reactants are, therefore, necessary in order to detect impurities.

For the determination of organic contaminations in salts, solutions of these salts can be prepared and subsequently measured using a TOC-L analyzer.



High salt concentrations generally present a problem for TOC analysis. These salts can crystallize in the combustion system and lead to higher maintenance needs.

In the case described below, the NPOC content of two salts was determined. The difficulty was the required detection limit of 10 mg/kg.

#### ■ Sample preparation

For sample preparation, 5 g of both salts (sodium nitrite and sodium nitrate) were weighed into a 50 mL volumetric flask and diluted with ultrapure water. During dilution, the solutions were acidified with concentrated sulfuric acid (25%).

Compound (Concentration)	Dilution	Conz.
Sodium nitrate (>99,9%)	Weighted Sample 5 g / 50 ml add. 1-2 drops Sulfuric acid until pH<7	approx. 10%
Sodium nitrite (>99,9%)	Weighted Sample 5 g / 50 ml add. 1-2 drops Sulfuric acid until pH<7 Caution: Nitrogen oxide gas is released	approx. 10%

Caution: Nitrite salts react to form of toxic nitrous gases. Sample preparation should, therefore, always be carried out under a hood. The samples should only be removed from the hood, when no more nitrous gases escape.

Calibration of the TOC-L system was done applying the automatic dilution function in the range of 0.5 mg/L to 10 mg/L.

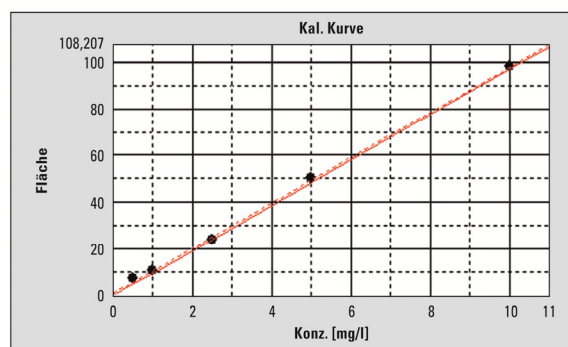
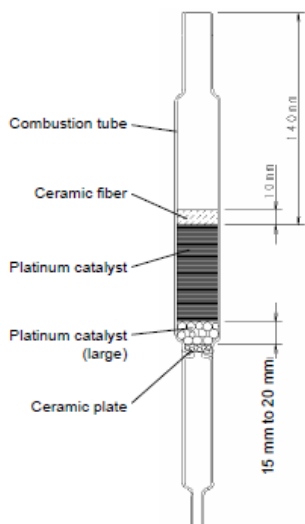


Fig. Multi-point calibration with dilution function

### ■ Kit for high-salt samples

The TOC-L series features a kit for high-salt samples, which significantly increases the instrument's availability. The kit consists of a combustion tube of a special geometry and a unique catalyst mixture.



In this application, sample acidification is carried out with sulfuric acid which is used to modify the sample matrix. Due to the higher melting point of  $\text{NaSO}_4$  (888 °C) compared to 801 °C of  $\text{NaCl}$  the lifetime of the combustion tube is longer.

### ■ Interferences

The combustion of nitrogen compounds can lead to the formation of nitrous oxide gas. Nitrous oxide exhibits absorption bands in the same IR detection range as  $\text{CO}_2$  and can, therefore, be misinterpreted for  $\text{CO}_2$ . In addition, nitrous oxide can cause tailing and can affect the peak symmetry.

A B-type scrubber is used to eliminate possible interference by nitrous oxide. Due to the high solubility of  $\text{N}_2\text{O}$  in water, the gas is dissolved in the B-type scrubber and will not reach the detector.

### ■ Results

The duplicate determination of the salt solutions yielded the following results:

Sample	NPOC [mg/kg]	RSD [%]
Sodium nitrate (>99,9%)	22,8	4,7
Sodium nitrate (>99,9%)	24,0	6,8
Sodium nitrate (>99,9%)	<10 (9,0)	-
Sodium nitrate (>99,9%)	10,2	5,4

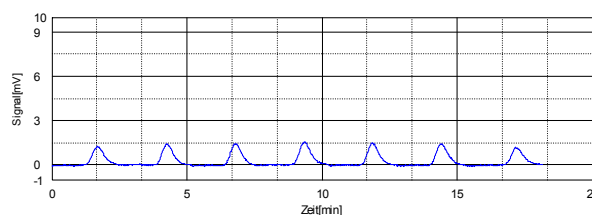


Fig. Example peaks: Sodium nitrate



### ■ Recommended Analyzer / Configuration

TOC-L<sub>CPH</sub>  
ASI-L  
High-Salt-Kit  
B-Type-Scrubber



## 4. TOC special applications

Due to its informative significance, the TOC sum parameter is widely applicable. It mirrors the total concentration of organically bound carbon or organic compounds.

In addition to the environmental, pharmaceutical and chemical industries, the TOC parameter is used in numerous other applications. The user's scientific curiosity and ingenuity often wants to solve an analytical problem or simplify complex analytics, and then finds the TOC as a key to the answer.

The TOC parameter can be determined easily and reliably. The experienced user

can control and calculate interferences that can be attributed to the matrix. Various options, kits and modules enable interference-free analyses in a wide range of applications.

With its TOC analyzers, Shimadzu offers flexible systems that can be modularly upgraded using various kits, modules and options. In this way, the TOC analyzer can be customized to the specific measurement task.

The possibility to detect and quantify all organic compounds within a simple analytical run always leads to new, often unusual, applications. Some only seem

to be useful for a one-time use while others seem to revolutionize entire analytical application areas.

Further information can be found in the individual application notes (for instance 'TOC determination in algae, liquid manure or carbon dioxide determination in beer'). In addition to TOC special applications, there are also application notes and information on 'Pharmaceutical industry', 'Chemical Industry', 'Environmental analysis', 'TOC in daily practice' and 'TOC process analysis.'



## Application News

**No.** SCA-130-401

Sum parameter – Total Organic Carbon

TOC\_determination in algal biomass –  
suspension method



The excessive global CO<sub>2</sub> emissions from the burning of fossil fuels (for instance in power plants) causes the search for climate-friendly uses of carbon dioxide.

One of the approaches for environmentally sound recycling is to convert the emitted CO<sub>2</sub> into biomass using photobioreactors.

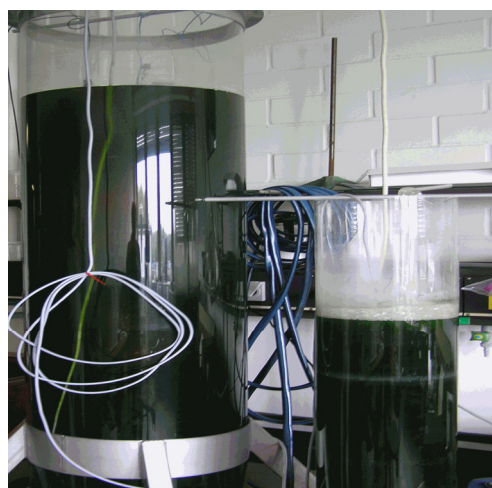
The CO<sub>2</sub> gas is introduced into the photobioreactor in order to be used for the growth of algae. The biomass, or algae, can be used in many different application areas: in the cosmetics industry, the construction industry, and the food segment, in agriculture as fertilizer or for energy utilization.

### ■ Test methods for implementation

The efficiency of the photobioreactors and the yield of growth are continuously monitored. To this end, various methods are available, including the determination of dry mass (gravimetric) or the photometric determination of chlorophyll (by absorption). These methods either require a high expenditure in terms of time and personnel, or they are nonspecific and inaccurate.

### ■ Innovative methods

To determine the biomass in the photobioreactor, a TOC analyzer was used. The carbon content of the 'algal soup' is directly proportional to the biomass.



### ■ TOC Measurement method

Depending on the type of algae used in the reactor, either the difference method or the direct method (NPOC) is suitable. In both cases, one should test which method will most accurately detect each particular type of algae. This can be compared with the results of the reference method.

Information on the analysis:

- calibration of the TC/NPOC and the IC parameters via the automated dilution function
- sample is generally measured undiluted
- injection volume: 90 µL
- at least 3 to 5 injections for statistical confidence
- rinse several times, depending on the sample

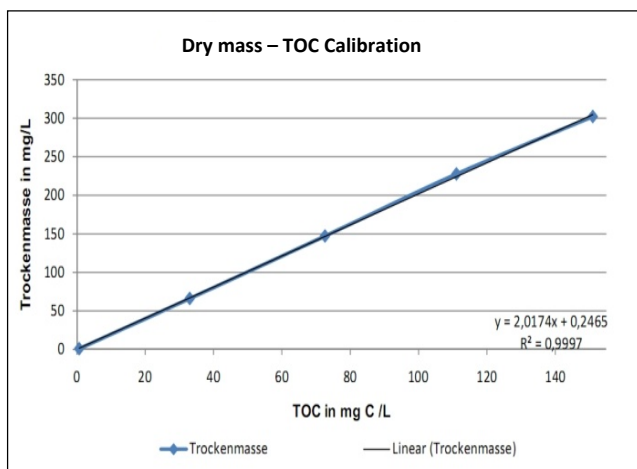
### ■ Sample preparation

The 4 – 10 µm large micro-algae of the *Chlorella vulgaris* species can be measured directly after sampling from the reactor without any further sample preparation. The difference method was used for the biomass determination. The method is suitable for all other single-cell algae that exhibit a stable carbon content under different growth conditions.

Using the difference method, the TC and TIC were determined and the TOC was subsequently calculated from these values. Calibration using the resulting dry mass of the algae makes it possible to draw conclusions on the dry biomass content in the sample from the TOC.

### ■ Correlation

The TOC correlation (algae biomass/TOC) must be determined for each type of algae specifically. It can also be calibrated against the determined dry mass.



First, the algae sample is measured and the TOC is determined. Subsequently, the sample is filtered through a 0.2 µm syringe filter and measured again in the TOC analyzer to be able to distinguish between the TOC content originating from the algae and the carbon content possibly originating from

the extracellular substances produced by the algae or released into the culture medium after the algae have died off. The TOC determined this way is the carbon content of the investigated algae. To draw conclusions on the dry mass yield, the percentage carbon content in the algae must be determined.

Several direct and indirect methods are available. The most simple and, at the same time, highly reliable method is to combust the washed and dried algae in a solid-matter TOC analyzer. A second method is to filter the algae, dry them and then determine their mass. In combination with TOC and photometry measurements, a correlation between the TOC value and the algal dry mass can be determined, which provides information on the carbon content of the algae. From the carbon mass fraction and the TOC value, the dry mass of the algae solution can be very accurately calculated.



### ■ Recommended analyzer / Configuration

TOC-L CPH  
ASI-L (40ml) with stirrer option and external Sparge-Kit

## Application News

**No.** SCA-130-402

Sum parameter – Total Organic Carbon

TOC\_determination in liquid manure and  
fermentation fluids  
– suspension method

Biogas is one of the energy sources of the future and can be used in the generation and supply of energy, or it can be fed into the natural gas networks in the form of biomethane. The generation of energy from renewable or regenerative energy sources, which include water, wind, solar and other types of biomass, replaces the use of fossil fuels.

For the production of biogas from, for instance, various liquid manures or maize silages, pretreatment methods for liquid manure and the optimization of the fermentation process and biogas yield are investigated.



Reactors with various volumes are used for production testing. The prepared liquid manure or mixtures of other substrates are used for fermentation. The generated biogas is diverted via pipelines, the resulting volume is pneumatically determined and the gas composition is analyzed.



Fig. Experimental setup to generate bio gas in the laboratory

### ■ Efficiency

To evaluate the efficiency of the reactor and the method, biogas was analyzed in different ways. An important parameter is the gas chromatographic determination of the methane content. In order to be able to compare the biogas yield of the various substrates, the biogas volume or methane volume was expressed in terms of the organic dry matter present in the substrate (NI/kg ODM). This requires the accurate determination of the initial concentration of the organic substance in the liquid manure.

For this determination, proven methods are available. First, the dry matter (DM) of the liquid manure is determined at 105 °C. The dried liquid manure is subsequently annealed to a constant mass at 550 °C in a muffle furnace. The loss of mass during annealing corresponds to the organic content of the liquid manure. The ratio of methane gas concentration and organic content corresponds to the biogas production yield (fermentation) and is a key criterion for the fermentation of different types of biomass and for the assessment of the efficiency of fermentation processes.

### ■ Innovative methods

In order to avoid long annealing times for the ODM determination, an alternative method for the determination of the organic substance was sought. The TOC suspension method was considered suitable for this purpose. The dried sample was weighed into an Erlenmeyer flask and mixed with hydrochloric acid to convert the inorganic carbon compounds, such as carbonates and hydrocarbonates, to carbon dioxide. In the next step, a dispersion device was used to break up and homogenize the suspension.



Fig. Homogenisation of the suspension

During this process, most of the generated carbon dioxide was also removed. The final solution is subsequently transferred into the autosampler vials of the analyzer and automatically analyzed. For this purpose, a small fraction is injected onto the 720 °C hot platinum catalyst. The organic substances are then converted into carbon dioxide and measured using an NDIR detector.

The advantage of this alternative method lies in its suitability for automation. This way, many samples can be processed automatically in sequence.

With the possibility of multiple injections, the method also offers statistical reliability. In the muffle furnace, a combusted weighed sample yields an ODM value. The suspensions are generally analyzed at least four times to establish a mean value.

### ■ NPOC-Determination

For the determination of the organic content in liquid manure (duplicate determination from two different approaches with each 5 separate injections) yielded the following results:

Liquid manure (dried and powdered)	NPOC [mass.- %]	RSD [%]
Sample 1	44,1	0,8
Sample 1	44,2	1,9
Sample 2	44,2	1,6
Sample 2	42,5	1,4

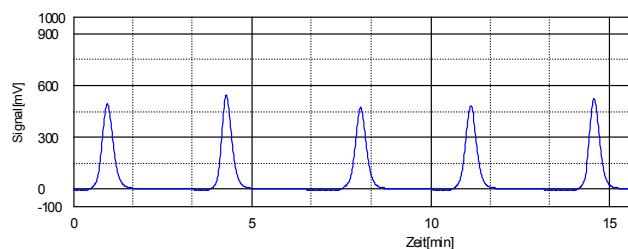


Fig. NPOC-Peaks of suspension



### ■ TN<sub>b</sub>-Determination

The TOC determination using catalytic combustion oxidation allows the simultaneous measurement of the total bound nitrogen (TN<sub>b</sub>), since, in addition to the carbon dioxide from organic substances, NO is formed from nitrogen-containing compounds. For the conversion of NO to NO<sub>2</sub>, the measuring gas ozone was fed to the chemiluminescence detector connected in-series. The photons emitted during this reaction are detected and are used in the calculation of the TN<sub>b</sub> value. Nitrogen compounds also play an important role when it comes to liquid manure.

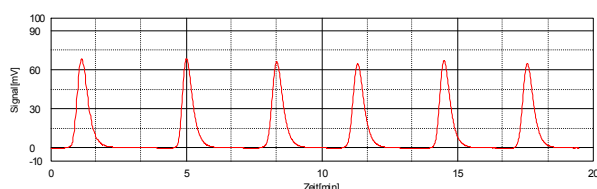


Fig.4: Peak graphs of TN-determination

Simultaneously with the organic content, the TN<sub>b</sub> was determined (duplicate determination from two different approaches with 5 separate injections each) yielding the following results:

Liquid manure (dried and powdered)	TN <sub>b</sub> [mass.-%]	RSD [%]
Sample 1	1,84	1,5
Sample 1	1,80	0,9
Sample 2	1,76	2,2
Sample 2	1,68	1,4

### ■ Conclusion

The TOC suspension method offers a good alternative for the fast, straightforward and accurate analysis of the organic content in liquid manure samples. The possibility for co-determination of the nitrogen content also enables users to acquire additional useful information for the evaluation of liquid manure samples.



### ■ Recommended Analyzer / Configuration

TOC-L<sub>CPN</sub> with normal sensitive Catalyst for TN<sub>b</sub>-Determination: TNM-L Module ASI-L (40ml) with stirrer option and external Sparge-Kit.

## Application News

Sum parameter – Total Organic Carbon

### Carbon dioxide determination in beer

**No.** SCA-130-403

Carbon dioxide is an important ingredient in many soft drinks. This is also the case for beer. It creates a sparkling and refreshing (tangy) taste and is important for the formation of foam.

The CO<sub>2</sub> content of a beer affects the threshold values for various fragrance and aroma components. In addition, bottling under CO<sub>2</sub> increases the shelf life of beer..



In the manual of the 'central- European brewery technological analysis commission' (MEBAK) various methods for the determination of CO<sub>2</sub> are listed. These are generally based on manometric or titrimetric method, or they are methods that use specialized detectors.

Disadvantages of these methods are often the lack of selectivity for CO<sub>2</sub> (other gases or substances are also determined), high expenditure in terms of personnel and time, and the lack of possibilities for automation.

In order to develop a method that does not have these disadvantages, a TOC analyzer was used.

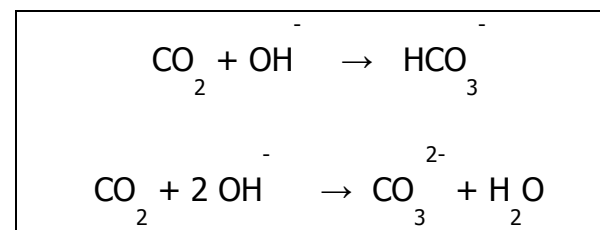
#### ■ Innovative methods

In this method, the sample (beer) is directly placed in a 40 mL autosampler vial. 5 mL of a 32% NaOH solution was added to the autosampler vial to preserve the CO<sub>2</sub>.

The sample is subsequently added directly to the autosampler and the IC (inorganic carbon) content is measured.

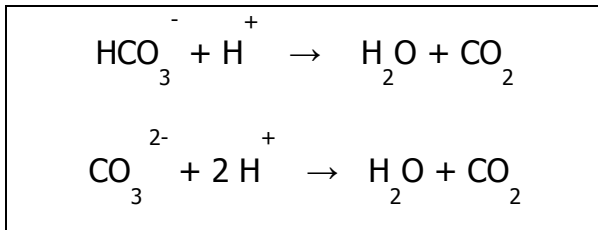


#### Preservation step:



In the TOC analyzer, the sample is injected in a concentrated phosphoric acid solution (25%). The CO<sub>2</sub> is subsequently released again and is transferred via the carrier gas to a CO<sub>2</sub>-selective NIDR detector where it is detected.

**Displacement reaction:** (the strong acid displaces the weak acid from its salt)



To calculate the results, the IC function of the TOC system is calibrated using a sodium hydrogen carbonate standard in the range of 100 – 1000 mg/L. The dilution of the individual calibration points is performed automatically via the dilution function of the instrument.

#### ■ Advantages of this method

- can be automated to a high degree
- fast
- good reproducibility and high accuracy (precision)
- multiple determinations from one sample is possible
- effortless calibration
- simple operation
- highly specific

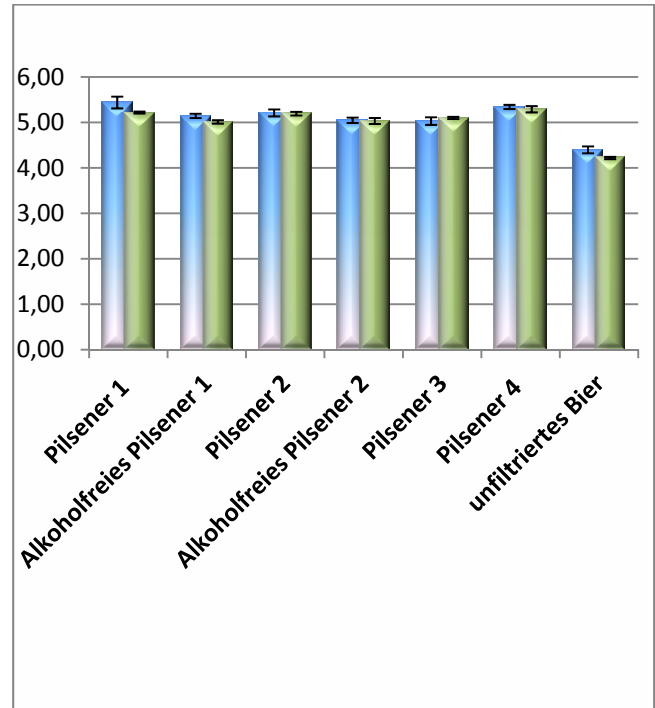
Using the modern TOC-L software, evaluation can be carried out automatically or can be recalculated manually. Another function enables further processing of the measurement results. This way the carbon dioxide content can be directly presented in the desired dimension. Due to the possibility for multiple injections, the evaluation contains all the important statistical quantities

Another sample preparation variant is to be carried out during the determination of carbon

dioxide in bottled or canned beer. In this step, 5 mL of a 32% solution of NaOH was directly added to the freshly opened bottle or can for preservation.

#### ■ Comparison of the methods

The following graph shows the good agreement between the TOC method (blue bars) and the Corning method (green bars).



#### ■ Recommended Analyzer / Configuration

TOC-L<sub>CPH</sub>  
ASI-L (40ml)



## 5. TOC in daily practice

As market leader in TOC analysis, Shimadzu connects tradition with experience. This enables users to profit from personal support or by attending seminars and user meetings organized by Shimadzu. These application-oriented meetings serve for the exchange of information and experiences.

In this particular field of application notes, specific sets of subjects 'TOC in daily practice' are listed that are not covered by one of the special applications. These are subjects that are related to the TOC parameter, independently of the matrix.

The wealth of experience in TOC analysis naturally finds its way into the devel-

opment of our TOC systems. Whether online analyzers or laboratory TOC systems – they all impress by their great flexibility, high availability, extreme robustness and stability, simple and intuitive operation and advanced operating and evaluation software. Many additional functions facilitate the user's work and provide more freedom for other important tasks.

This chapter also applies to the individual modules, kits or options of Shimadzu's TOC analyzers. Useful functions are also described.

Further details are available in the individual application notes (for instance 'TOC determination methods', 'Total

nitrogen determination' or 'Blank values'). In addition to the information on 'TOC in daily practice', there are also application notes on 'Pharmaceutical industry', 'Chemical Industry', 'TOC special applications', 'Environmental analysis' and 'TOC process analysis.'



## Application News

Sum parameter – Total Organic Carbon

### TOC – Determination methods according to EN 1484

**No.** SCA-130-501

The EN 1484 standard “Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)” defines various terms and parameters.

#### ■ Definitions according to EN 1484

**TC:** Total carbon – the sum of organically bound and inorganically bound carbon present in water, including elemental carbon.

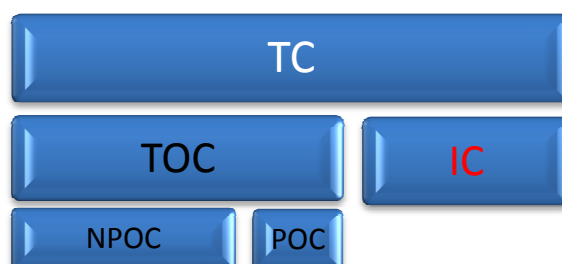
**TIC:** Total inorganic carbon – the sum of carbon present in water, consisting of elemental carbon, carbon monoxide, carbon dioxide (also carbonates and hydrogen carbonates), cyanide, cyanate, and thiocyanate. TOC instruments mainly detect CO<sub>2</sub>, originating from hydrogen carbonates and carbonates, just like TIC.

**TOC:** Total Organic Carbon – organically bound carbon present in water, bonded to dissolved or suspended matter. Cyanate, thiocyanate and elemental carbon are also determined.

**POC:** Purgeable Organic Carbon – the TOC content that is purgeable under the conditions of this method.

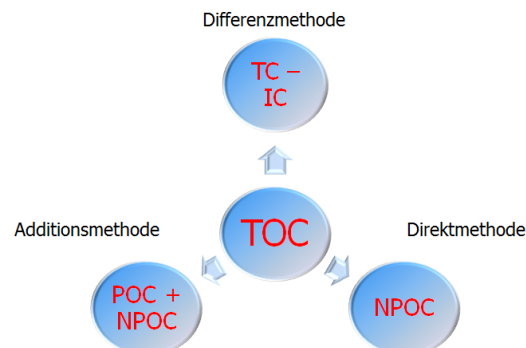
**NPOC:** Non Purgeable Organic Carbon – the TOC content that is not purgeable under the conditions of this method.

The following graph shows how the parameters are linked:



#### ■ Determination methods

The TOC can be determined according to three different methods:



#### ■ Difference method

For the difference method, the parameters TC and IC are measured. The TOC is then determined by way of calculation.

**TC:** The analysis of the total organic carbon is carried out via oxidation (thermal or wet-chemical) and subsequent determination of the resulting carbon dioxide using NDIR detection.

**TIC:** Through acidification of the sample using a mineral acid at room temperature and subsequent NDIR detection of the expelled carbon dioxide the inorganic carbon is detected.

The TOC is calculated from the difference between TC and TIC:  $TOC = TC - TIC$

#### ■ Limitations of the difference method

The inorganic carbon content may not be too high in comparison to the TOC.

Error propagation can result in a high level of uncertainty for the calculated TOC value. The EN 1484 standard recommends that the TOC value, when using the differential method, should be higher or equal to the TIC value ( $TOC \geq TIC$ ).

#### Example:

TC – Value = 100 mg/l (RSD = 2%)  $\pm$  2 mg/l  
(98 – 102 mg/l)

IC – Value = 98 mg/l (RSD= 2%)  $\pm$  1,96 mg/l  
(96,04 – 99,96mg/l)

TOC = 2 mg/l  $\pm$  3,96mg/l (- 1,96 - 5,96 mg/l)

Due to error propagation, the total error is  $\pm$  3.96 mg/L.

According to the difference method, the error of the total result is larger than the calculated TOC content! In the worst case, this can result in a negative TOC value.



#### ■ Addition method

For the addition method, the parameters POC and NPOC are measured. The TOC is then calculated.

**POC:** Degassing of the volatile compounds with subsequent catalytic combustion at 680°C and determination of the resulting carbon dioxide using NDIR detection.

**NPOC:** Measurement of the non-purgeable organic compounds, after POC analysis using catalytic combustion at 680°C and subsequent determination of the resulting carbon dioxide using NDIR detection.

The TOC is calculated via addition:

$TOC = POC + NPOC$

#### ■ Direct method

For the direct or NPOC method, it is assumed that the sample does not contain any significant amounts of volatile or purgeable organic compounds. According to this assumption, the TOC is directly determined as NPOC.

**NPOC:** Acidification of the sample using a mineral acid (for instance HCL) to a pH < 2, whereby carbonates and hydrogen carbonates are completely converted to carbon dioxide. The carbon dioxide is removed from the sample solution via a sparge gas. Direct NPOC measurement (similar to TC measurement) via oxidation to CO<sub>2</sub>. Subsequent NDIR detection.

The TOC corresponds to the NPOC:

$TOC = NPOC$

## Application News

### No. SCA-130-502

Sum parameter – Total Organic Carbon

### Determination of the purgeable organic carbon (POC)

According to EN 1484, which contains the instructions for TOC determination, the POC (purgeable organic carbon) is the TOC content that can be expelled under the conditions of this method. This information is very unspecific and should be described here in more detail.

The instruments in the TOC-L series can be extended with an option to include measurement of the POC parameter. The core feature of this option is the LiOH trap, which is placed in the flow line of the analyzer.



For POC determination, the sample is aspirated using the TOC-L injection syringe, acidified with HCL and subsequently purged using carrier gas. In this step, CO<sub>2</sub> originating from carbonates and hydrogen carbonates as well as all volatile organic compounds (POC) are purged from the solution. The LiOH trap binds the CO<sub>2</sub> from the gas mixture (originating from the TIC). The volatile compounds pass the trap and reach the catalyst.

Here, the volatile organic compounds are converted to CO<sub>2</sub> and detected via NDIR detector.



Fig. The addition method (NPOC + POC)

During the course of the addition method, the remainder is used for NPOC determination. However, in the drinking water application or ultrapure water application, the POC content is completely negligible. Here, TOC = NPOC

The POC can, nevertheless, play an important role in wastewaters, particularly in industrial effluents.

#### ■ Calibration

Particular attention should be paid to calibration of the POC. Standards that are prepared with volatile, purgeable organic substances are inherently very unstable. This is why IC standard solutions (prepared from carbonates and/or hydrogen carbonates) are used for POC calibration. Sampling of the IC solutions for POC determination is carried out using the TOC-L injection syringe. The IC solution is acidified in the syringe. The inorganic substances of the standard solution are converted to CO<sub>2</sub> and transferred to the NDIR detector using a carrier gas.

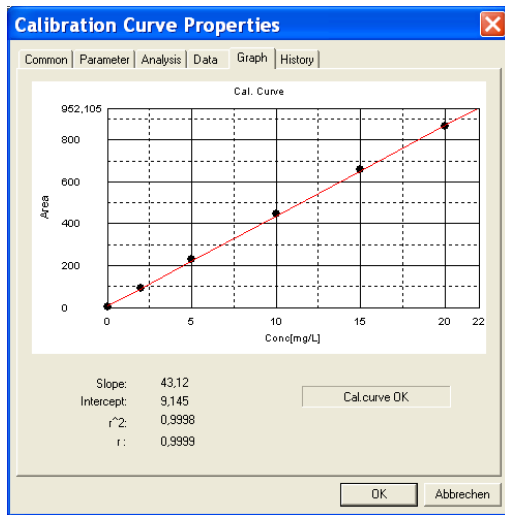


Fig. POC-Calibration with IC-standard

### ■ System testing

In POC analysis, it is of great importance that the LiOH trap functions perfectly. A test should, therefore, be carried out to confirm the efficiency of the CO<sub>2</sub> trap. This test should be carried out each working day:

An IC control solution (TIC = 1000 mg/L) is prepared and analyzed as a POC sample. For efficient functioning of the LiOH trap, the POC measuring result must be < 0.1 mg/L.

### ■ Example of a POC measurement

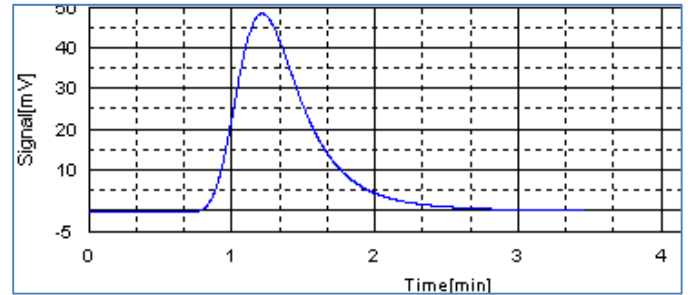
Sample: Toluene in ultrapure water

Toluene is a compound that is fully purgeable. In the addition method, the toluene sample is completely determined as POC.

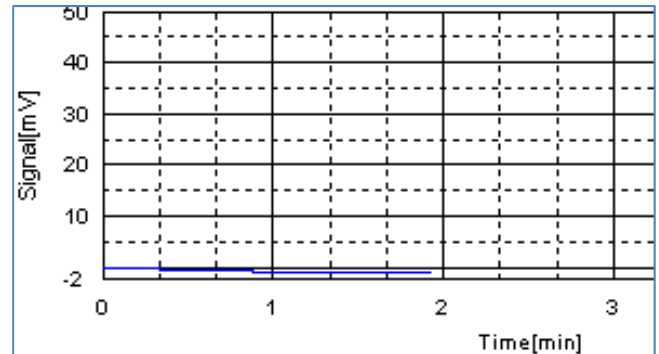
### POC measuring method:

Injection volume: 800 µL  
Purging time: 3 min

### POC-Peak:



### NPOC-Peak:



### Result:

TOC=4,05mg/l

POC=4,05mg/l => 100%

NPOC=0mg/l

### ■ Recommended Analyzer / Configuration

TOC-L<sub>CXX</sub>  
ASI-L  
POC-Option



## Application News

Sum parameter – Total Organic Carbon

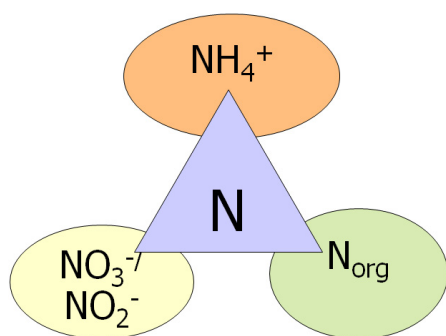
TN<sub>b</sub> – total bound nitrogen

### No. SCA-130-503

Although nitrogen compounds are essential for nature and the environment, high nitrogen depositions can lead to problems. Nitrogen compounds enter the environment primarily through agricultural processes. Nitrogen-containing fertilizers constitute the largest proportion. But nitrogen compounds can also enter the environment via chemical industrial processes.

Excessively high concentrations of nitrogen compounds in the environment can cause eutrophication of water bodies. Eutrophication is the process of uninhibited growth of algae and other organisms due to an excess supply of nutrients. This overgrowth results in a lack of oxygen in the water, which can lead to fish mortality and to the formation of aquatic dead zones.

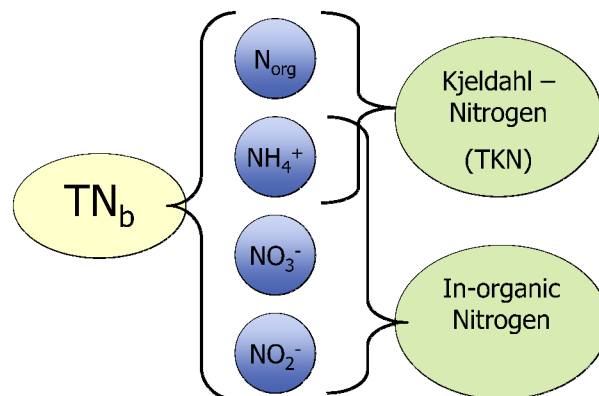
Bound nitrogen occurs in nearly all waters, mostly in the form of ammonia, nitrate, nitrite or organic compounds.



#### ■ Total nitrogen TN<sub>b</sub>

The variety of possible nitrogen compounds necessitated the definition of a sum parameter that represents the total nitrogen compounds. For this purpose, the so-called TN<sub>b</sub> (total bound nitrogen) was defined and standardized.

The TN<sub>b</sub> is the total nitrogen content of a sample in the form of ammonium, nitrite, nitrate, as well as organic compounds. The TN<sub>b</sub> does not include dissolved or gaseous nitrogen (N<sub>2</sub>). A differentiation between inorganic and organic nitrogen compounds is, by definition, not possible.



#### ■ Determination according EN 12260

EN 12260 describes the determination of nitrogen in the form of free ammonia, ammonium, nitrite, nitrate and organic compounds that can be converted under the described oxidative conditions.

The conversion of the nitrogen containing compounds takes place via combustion in an oxygen atmosphere higher than 700 °C to nitrogen oxide, which reacts with ozone to activated nitrogen dioxide (NO<sub>2</sub>\*). In the subsequent reaction to NO<sub>2</sub>, light quanta are emitted (chemiluminescence) that are measured by the detector.

#### ■ Simultaneous TN determination using the TNM-L

Based on the similar oxidation process, the TN<sub>b</sub> determination can be carried out simultaneously with the TOC measurement. For this application, the TNM-L option is installed on the top of the main TOC-L system.



Fig. TOC-L CSH with TNM-L Modul

The benefit is that no additional laboratory space is required.

For the simultaneous determination, the sample is injected onto the catalyst at 720 °C. All carbon atoms present in the sample are converted to CO<sub>2</sub> and, in parallel, the nitrogen atoms to NO. The gas mixture is then transported by the carrier gas stream through the NDIR detector, where the carbon dioxide content is measured.

Subsequently, the gas mixture enters the chemiluminescence detector, connected in series, where the nitrogen content is determined (See Figure below).

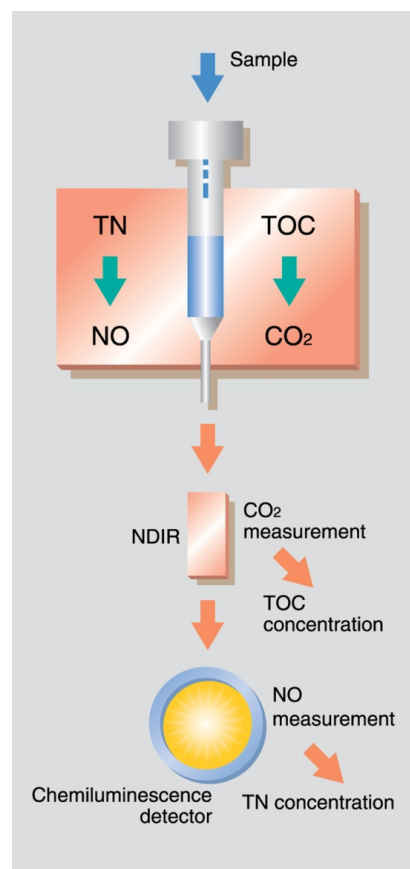


Fig. Simultaneous TOC/TN-Determination

It should be noted that an optimal injection volume must be selected for both parameters.

#### ■ Recommended Analyzer / Configuration

TOC-L<sub>CXX</sub> with TNM-L  
ASI-L

## Application News

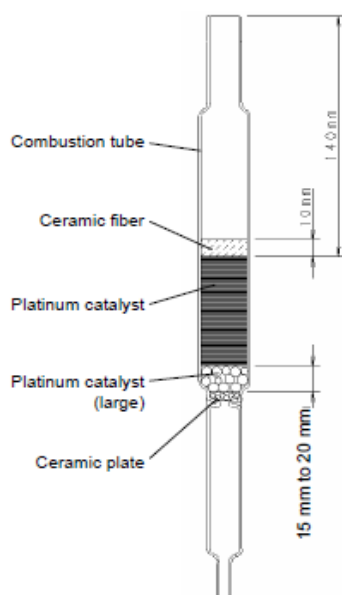
Sum parameter – Total Organic Carbon

Kit for high-salt samples

**No. SCA-130-504**

Samples with high-salt loads generally are a problem for TOC analysis. The problem is less the conversion of organic compounds to CO<sub>2</sub> than the effects of the salt on the catalyst. This leads to higher maintenance needs, as the salt can crystallize in the combustion system.

In many applications for the instruments in the TOC-L and the TOC-4110/4200 series, the kit for salt-containing samples is an important component. It consists of a combustion tube of a special geometry and a unique mixture of catalyst beads.



### ■ Sample preparation

In this application, sample acidification is carried out with sulfuric acid which is used to modify the sample matrix.

While NaCl has a melting point of 801 °C, the melting point of Na<sub>2</sub>SO<sub>4</sub> is higher (888 °C). The potassium salts of sulfuric acid also have a significantly higher melting point than those of hydrochloric acid. This has a positive effect on the lifetime of the combustion tube.

Compound	Melting point
NaCl	801°C
KCl	773°C
Na <sub>2</sub> SO <sub>4</sub>	888°C
MgCl <sub>2</sub>	708°C
CaCl <sub>2</sub>	782°C
K <sub>2</sub> SO <sub>4</sub>	1.069°C

Tab. Melting point of different salts

Results indicate that the stability of the catalyst is increased, and that up to 12 times the number of samples can be measured before the catalyst must be exchanged and the instrument needs servicing.



Fig. Catalyst filling

### ■ Endurance test

To determine the performance of this option, a brine solution was measured in a long-term test. For this purpose, a 28 % NaCl solution (matrix adapted with a 15 % sulfuric acid solution and spiked to a 5 ppm TOC solution using a KPH solution) was injected 220 times. Initially, a blank value and a control standard with 10 ppm TOC were measured. The control standards were tested after 110 and 220 injections, respectively. The injection volume was 50  $\mu$ L.

The following figure shows the excellent reproducibilities and the stability of the measurement.

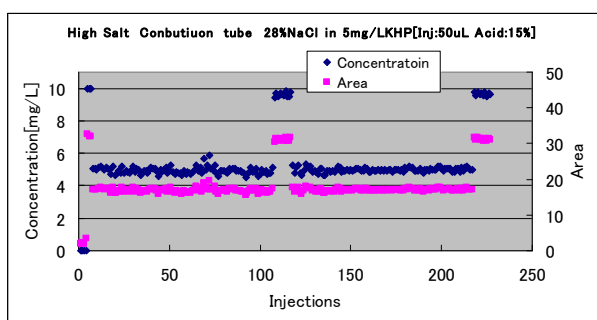


Fig. Results of endurance test

### ■ Related application

The high-salt kit is used for many different applications in order to keep the maintenance need for difficult matrices as low as possible.

Examples:

- 104 TOC-Determination in seawater
- 304 TOC-Determination in brine solution
- 306 TOC-Determination in soda solution
- 308 TOC-Determination in sodium nitrate
- 603 TOC-Determination in chemical industry



### ■ Recommended Analyzer / Configuration

TOC-L cxx

ASI-L

Kit for high-salt samples

B-Type Scrubber

(At very high halogen concentrations in the matrix, the B-type scrubber is recommended. This scrubber protects the detector cell of the NDIR detector.)



## Application News

**No.** SCA-130-505

Sum parameter – Total Organic Carbon

Kit for small sample volumes

The instruments of the TOC-L series are designed to successively analyze many different types of samples of different concentrations. For the autosampler, sample trays for different sample numbers and sample volumes are available.



To eliminate cross-contamination between analyses of the different samples, the number of rinsing steps can be defined in the software. There is usually enough sample volume available to rinse the tubing and the injection system of the TOC-L several times. Depending on the measuring method, injection volume, measurement range and rinsing steps, 10 – 20 mL of the sample is needed.

### ■ Small sample volumes

It can also occur, however, that only a few mL of sample are available. This is usually the case when there is only little sample available, the sampling process is complex or the sample is very valuable. For such cases, the kit for small sample volumes is available. The 5 mL syringe body can be exchanged for a 500 µL syringe in a rapid conversion step. Moreover, the injection slider has to be exchanged too.

### ■ Specification

With this option, automatic dilution, acidification and sparging is not possible and the specifications are, therefore, changed as follows:

Measurement range: TC, IC: to 2,000 mg/L

TN: to 200 mg/L

Injection volume: 150µl maximal

Diameter: 0.2 mm

NPOC-Measurement: In ASI-L with external  
Sparge kit

ASI-L: 9ml Rack

### ■ Example

5 mL sample is sufficient for NPOC determination using an ASI-L, 9mL vials (3 injections with 150 µL injection volumes)

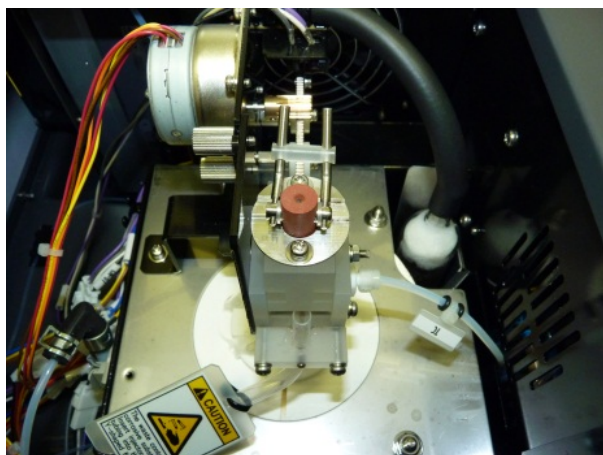
## Application News

**No.** SCA-130-506

Sum parameter – Total Organic Carbon

Kit for manual injection

The manual injection kit enables the analysis of water samples and gases. The sample for TC determination is directly injected into the combustion chamber using a  $\mu\text{L}$  syringe. This is interesting for applications where only a very small sample volume is available.

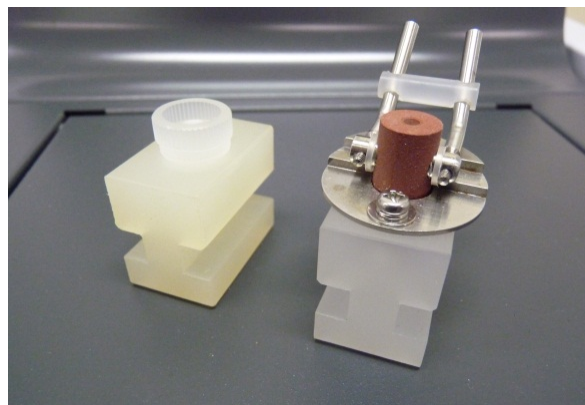


The kit for small sample volumes is a module for TOC analyzers that can be used for automated sample preparation and analysis of small sample amounts. The methods can be optimized in such a way that only a few mL of the sample are required. Optimization should, however, not be at the expense of the intermediate rinsing step.

When even smaller amounts than the few milliliters are available, the TOC-L user can fall back on the manual injection kit.

For gas samples, a distinction can be made between total carbon (for instance  $\text{CO}$  or  $\text{CH}_4$ ) and  $\text{CO}_2$ .

The kit consists of two injection blocks, which can be easily installed in the TOC system. One of the injection blocks is used instead of the IC-port; the other block replaces the TC injection block.



This conversion does not take longer than one minute.

### ■ Specification

For liquid samples:

Measurement range: TC, IC: to 20.000 mg/L  
Injection volume: 150 $\mu\text{L}$  maximal  
Measurement time: TC, IC: 3 minutes  
Reproducibility: RSD: 2%  
(over 8.000mg/L: 3% )

For gas samples:

Measurement range: 6ppm to 100%  $\text{CO}_2$   
Injection volume: 20 $\mu\text{L}$  bis 10mL  
Measurement time: 2 – 4 Minuten  
Reproducibility: RSD: 2%

# Application News

No. SCA-130-507

Sum parameter – Total Organic Carbon

## Calibration with automatic dilution function



The core feature of the TOC-L series is the ISP module (Integrated Sample Pretreatment). The ISP module consists of an 8-port valve and a syringe with sparging gas connector. In addition to acidification and sparging in the syringe, the system enables automated dilution. This allows for the wide measuring range, dilutes highly polluted samples and enables the creation of dilution series from a stock solution. The various possibilities offered by the ISP module thus reduce the time expenditure by the user.

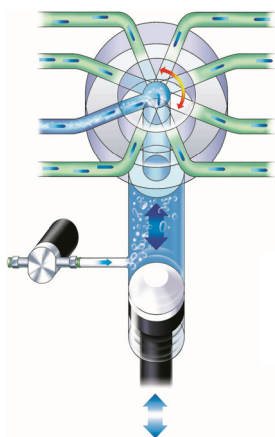
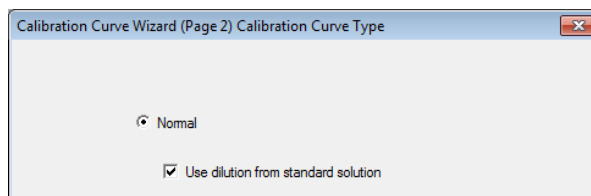


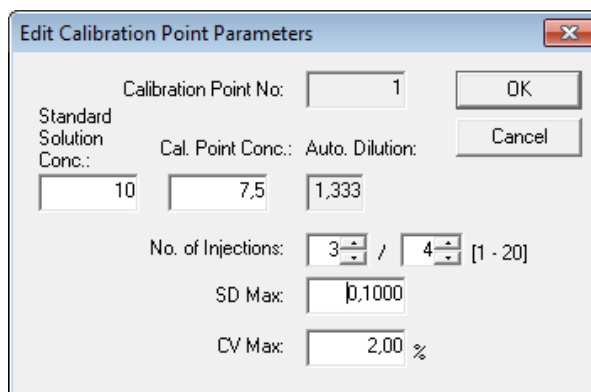
Fig. ISP-Module of TOC-L series

### ■ Calibration with automatic dilution function

To create calibration curves, the dilution function is activated via the wizard:



When filling the data of the calibration points, the concentration of the standard solution (stock) is entered first, followed by the desired calibration curve point. The software calculates the required dilution factor:

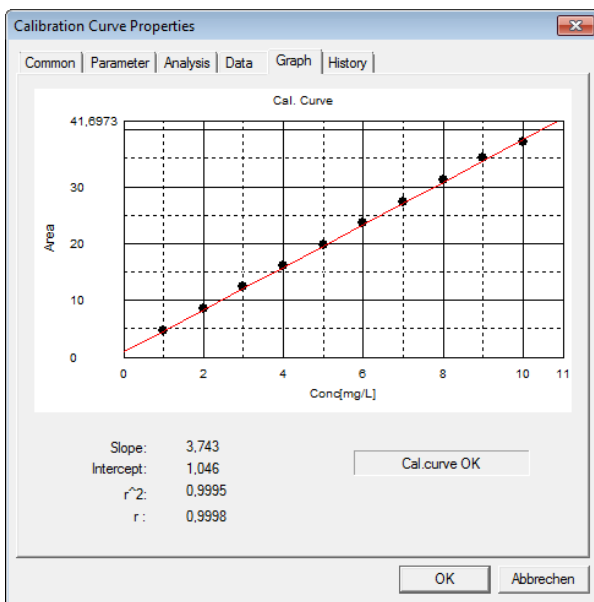


Since fractional factors are allowed, it is possible to create a 10-point calibration curve with equidistant concentration intervals from one standard solution.

The following figure shows the list of calibration points of a 10-point calibration curve in the range of 1 to 10 mg/L:

No.	Conc.	Auto...	Std. Sol. Co...	Mean Area	No. of Inj.	Excluded
1	1,000 mg/L	10,00	10,00 mg/L	4,679	3/4	
2	2,000 mg/L	5,000	10,00 mg/L	8,464	3/4	
3	3,000 mg/L	3,333	10,00 mg/L	12,34	3/4	
4	4,000 mg/L	2,500	10,00 mg/L	16,00	3/4	
5	5,000 mg/L	2,000	10,00 mg/L	19,68	3/4	
6	6,000 mg/L	1,667	10,00 mg/L	23,60	3/4	
7	7,000 mg/L	1,429	10,00 mg/L	27,34	3/4	
8	8,000 mg/L	1,250	10,00 mg/L	31,28	3/4	
9	9,000 mg/L	1,111	10,00 mg/L	35,01	3/4	
10	10,00 mg/L	1,000	10,00 mg/L	37,91	3/4	

The measured calibration curve exhibits a linear range with a very good correlation coefficient ( $r = 0.9995$ ).

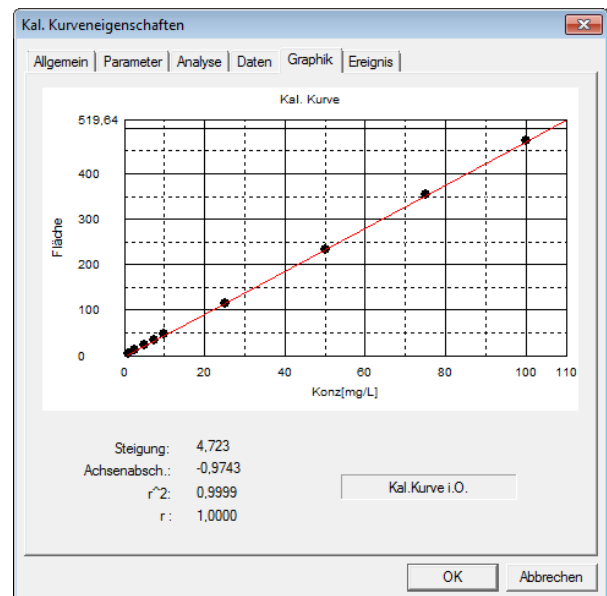


### ■ Calibration with automatic dilution function over two decades

In addition, there is the possibility to use different standard solutions for the dilution. Calibration was carried out from 1 to 100 mg/L using two standard solutions (10 and 100 mg/L).

Nr.	Konz.	Aut. Ve...	Std. Lsgl. Ko...	MW Fläche	Anz. Inj.	Ausgeschl.
1	1,000 mg/L	10,00	10,00 mg/L	4,944	3/4	
2	2,500 mg/L	4,000	10,00 mg/L	11,73	3/4	
3	5,000 mg/L	2,000	10,00 mg/L	22,92	3/4	
4	7,500 mg/L	1,333	10,00 mg/L	34,86	3/4	
5	10,00 mg/L	1,000	10,00 mg/L	46,26	3/4	
6	25,00 mg/L	4,000	100,0 mg/L	114,8	3/4	
7	50,00 mg/L	2,000	100,0 mg/L	232,8	3/4	
8	75,00 mg/L	1,333	100,0 mg/L	354,1	3/4	
9	100,0 mg/L	1,000	100,0 mg/L	472,4	3/4	

Also here, the measured calibration curve exhibits a linear range with a very good correlation coefficient ( $r = 0.9995$ ).





## Application News

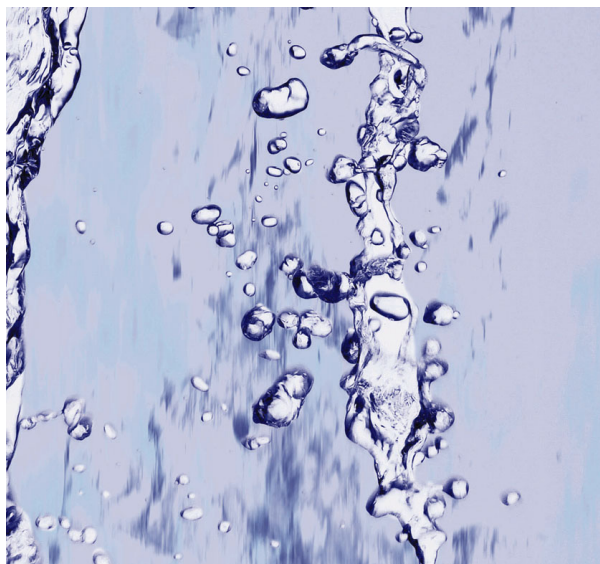
Sum parameter – Total Organic Carbon

### Blank value consideration in TOC analysis

**No. SCA-130-508**

Water plays a dual role in TOC trace analysis. On one hand, it is applied as a measuring medium and consumable in the TOC analyzer. It is used to prepare standards and to rinse the instrument. The automatic dilution function of the TOC-L uses ultrapure water for dilution of the samples or the standard solutions for multi-point calibration.

On the other hand, ultrapure water is a sample type in TOC analysis. In ultrapure water applications, including the analysis of water for injection and cleaning validation, ultrapure water samples are analyzed to determine their organic impurities.



For the determination of low concentrations at the trace-level, knowledge on the blank value is essential. The blank value is usually composed of several components. First, there is the instrument blank, secondly residual concentrations can occur in the solvent and in the reagents used. The influence of the blank value is particularly significant in TOC analysis, as carbon compounds are present everywhere and a widespread carbon input can, therefore, not be prevented.

With careful sample preparation and analysis, this blank value can be minimized and reliably determined. The blank value consideration and the analysis of a system blank value is only useful in very low concentration ranges of < 1 mg/L.

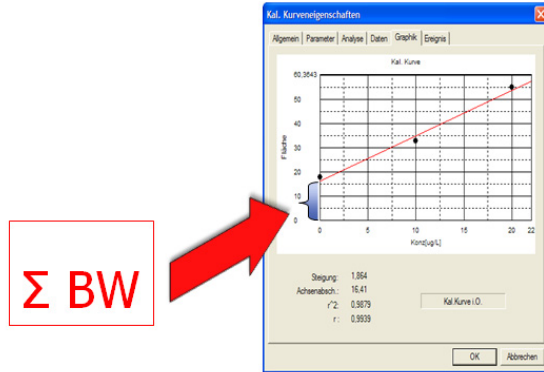
Purified waters that have been produced using highly complex water treatment systems, have different water grades. The DIN ISO 3696 standard specifies the requirements and test methods for water for analytical use and classifies these waters according to 3 grades.

<i>Parameter</i>	<i>Pure water Typ III</i>	<i>Pure water Typ II</i>	<i>Ultra pure water Typ I</i>
Ions, resistance (MΩ.cm)	>0,05	>1,0	>18,0
Ions, resistance (μS/cm)	< 20	<1,0	<0,055
<b>Organix, TOC (ppb)</b>	<b>&lt;200</b>	<b>&lt;50</b>	<b>&lt;10</b>
Pyrogene (EU/ml)	NA	NA	<0,03
Particle >0,2μm (U/ml)	NA	NA	<1
Bacteria (KBE/ml)	<1000	<100	<1

Tab 1: specification according to DIN ISO 3696

### ■ Blank value considerations

When, for instance, the NPOC is calibrated in the lowest concentration ranges, a positive area value for the zero value of the x-axis generally results, as well as a positive value of the y-axis where it intercepts the x-axis.



This positive area value reflects the blank value. This blank value is, however, not attributable to a specific factor or a specific cause but appears as the sum of the various blank value factors. This sum can consist of the following:

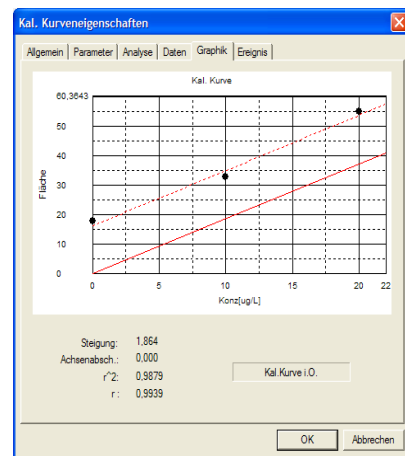
- Total blank value =  $\Sigma$  of
- + Blank value of the instrument
  - + Reagent impurity
  - + Blank value of the standard (ultrapure water)
  - + Contaminations from the environment (dust, contaminations on the glassware, etc.)

The calibration is evaluated according to the general straight-line equation:  
 $y = m \cdot x + b$

- y = Peak area
- x = TOC – concentration
- m = slope of calibration
- b = intercept

When a blank sample is now measured against this curve, the concentration 0 mg/L is obtained or, if the ultrapure water used is slightly cleaner, even a negative concentration value.

Both situations only describe the ratio between the actual blank value and the blank value when the calibration curve has been created. To obtain an absolute concentration value, there is the possibility of zero offset. The zero offset is a parallel offset of the calibration curve through the zero point. Through this offset, the absolute term (b) of the curve is set to zero and the blank value (positive intercept) of the calibration is taken into consideration in the sample analysis.



While the concentration in ultrapure water for the preparation of standard includes a blank value, the carbon concentration in an ultrapure water sample only reflects the actual TOC concentration of the sample.

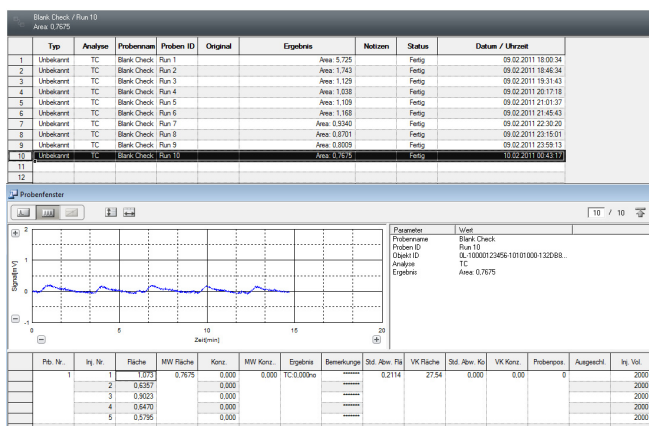
In short: dilution water has a blank value, a sample does not have a blank value.



**■ Instrument blank value**

Due to the ubiquity of certain compounds, potential minute leaks in the instrument and possibly persistent deposits or biofilms, can lead to area values that originate from the instrument itself and not from the measured sample. To determine this value, the ‘blank check’ procedure can be performed:

For this purpose, the system (TOC-LCPH) carries out an automatic analysis of circulating ultrapure water. The resulting condensation is collected in a suitable container inside the instrument. As soon as enough condensed water is available, the water is circulated, i.e. it is injected again. This procedure is carried out 50 times and it can, therefore, be assumed that the final determined area value corresponds to the actual instrument blank value.



Note: The determination of the instrument blank value is also suitable for intensive cleaning of the flow lines and for the ‘breaking in’ a newly built-in catalyst. As this is a very time consuming method, it should preferentially be carried out overnight.

**■ Reagents – blank value**

Reagents, such as hydrochloric acid, often stand unobserved and unintentionally next to the instrument for months and absorb vast amounts of organic carbon from the environment (‘from a blank value perspective’). For the determination of such reagent blank values, the standard addition method is suitable.

**■ Contaminations from the environment**

At last, the blank value is discussed that can arise from everywhere in the environment and can enter the analysis from various sources. People and their industrial landscapes are the source of a large variety of organic carbon compounds. Humans themselves consist of 18.2 % organic carbon and lose, for example, 1 – 2 g skin particles per day. These generally settle in the form of house dust.

In addition to carbon originating from our own bodies, carbon sources present in cosmetics or toiletries such as soaps, deodorants, perfumes, after-shaves skin creams, ointments, plays an important role. Also the laboratory harbors large sources of organic carbon compounds.

Room air contains numerous pollutants that can easily bind to dust particles and can therefore also be present in house dust. Finally, it should not be overlooked that room air contains approximately 0.4 vol% / 0.06 mass% (400 / 600 ppm) CO<sub>2</sub>.



## Application News

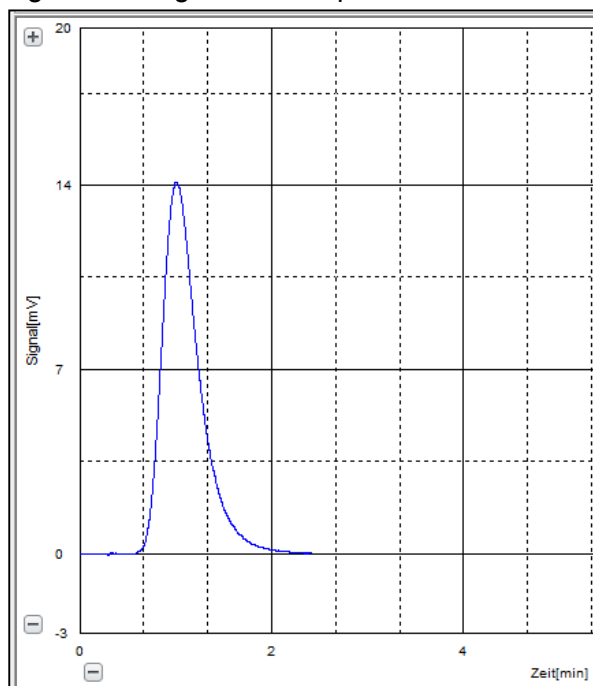
No. SCA-130-509

Sum Parameter – Total Organic Carbon

TOC – Measurement principle  
Catalytic combustion at 680°C

### ■ TOC-Measurement principle

The organic carbon compound is oxidized by combustion to carbon dioxide. The carrier gas (transporting the CO<sub>2</sub>) is cooled and dehumidified and passed through a halogen scrubber into the cell of the NDIR (Non Dispersive Infrared) detector where the CO<sub>2</sub> is detected. The NDIR outputs a detection signal which generates a peak.



### ■ Peak detection

In the past high temperatures (up to 1000°C) were necessary because the first TOC instruments use the peak height for integration. Due to this the conversion to CO<sub>2</sub> must be instantaneous to keep the peak as narrow and sharp as possible.

### ■ Disadvantage of high temperature

The very high combustion temperature has the disadvantage of high levels of maintenance (deactivation of catalyst, corrosion of combustion tube and detector cell) due to the salt melt products.

Salt interference at the detection cell from the salt melt products may impact the quality and accuracy of the data. Maintenance time is also increased due to the extended cool down and reheating time required based on the higher combustion temperature.

### ■ Shimadzu TOC method

Shimadzu developed the catalytically oxidation at 680°C and uses peak area for integration. This temperature is lower as the melting points of some salts:

Compound	Melting point
NaCl	801 °C
KCl	773 °C
Na <sub>2</sub> SO <sub>4</sub>	888 °C
MgCl <sub>2</sub>	782°C
CaCl <sub>2</sub>	782 °C

Tab. Melting points of different salts

The deactivation of the catalyst and the corrosion of the combustion tube are minimized. In total the maintenance request is lower as using higher temperature. On the other hand the platinum catalyst ensures a complete oxidation of all organic compounds.





■ Recovery rates with 680°C combustion technique

Compound	Prepared [mg/L]	Measured [mg/L]	Recovery [%]
Ethanol	200.0	201.2	100.6
2-Propanol	50.0	49.8	99.6
1-Pentanol	166.2	166.6	100.2
1-Hexanol	172.5	173.0	100.3
Dimethyl-formamide	139.5	141.5	101.4
Glucose	200.0	200.4	100.2
Sucrose	200.0	197.5	98.8
Sucrose	50.0	49.9	99.8
Sucrose	2.000	1.968	98.4
Fructose	50.0	49.9	99.8
Dodecyl-benzene sulfonic acid	55.0	56.0	101.8
L-glutamic acid	50.0	50.1	100.2
Tartaric acid	50.0	49.8	99.6
Citric acid	50.0	49.6	99.2
Tannine	47.0	47.4	100.9
Lignin	48.3	47.7	98.8
Albumin	44.5	44.1	99.1
Humic acid	44.7	45.3	101.3
Caffeine	50.0	49.5	99.0
1,10-Phenanthroline	50.0	49.7	99.4
Catechin	50.0	49.1	98.2
1,4-Benzoquinone	100.0	100.4	100.4
Sodium acetate	100.0	98.3	98.3
Nicotinamide	200.0	198.9	99.5
Nicotinamide	100.0	101.3	101.3
Nicotinamide	2.000	1.993	99.7

Compound	Prepared [mg/L]	Measured [mg/L]	Recovery [%]
Urea	200.0	203.0	101.5
Urea	2.000	1.986	99.3
Ethylurea	100.0	102.3	102.3
Thiourea	200.0	201.8	100.9
Thiourea	2.000	1.973	98.7
Nicotinic acid	200.0	198.5	99.3
Nicotinic acid	2.000	1.932	96.6
Sulfanilic acid	200.0	199.3	99.7
Sulfanilic acid	2.000	1.969	98.5
Sulfosuccinic acid	52.7	53.0	100.6
Cyanuric acid	10.10	10.55	104.5
Acrylamide	8.36	8.61	103.0
Pyridine hydrochloride	200.0	197.1	98.6
Pyridine hydrochloride	2.000	1.983	99.2
Quinine hydrochloric	200.0	202.3	100.4
Quinine hydrochloric	2.000	2.008	100.8
Cellulose (insoluble)	100.0	98.6	98.6
Poly-styrene (insoluble)	3.00	2.99	99.7

**Note:** The recovery rate is effected by sample preparation, instrument condition and surrounding circumstances!



## 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 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.

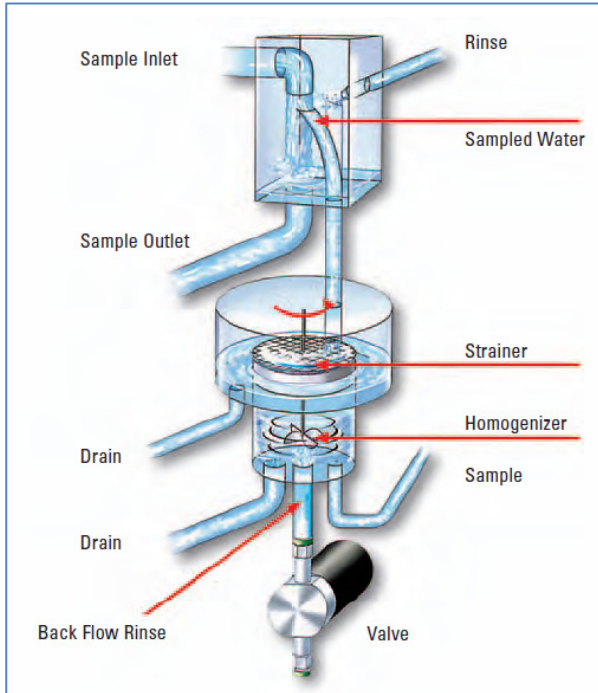


Fig. Multi-Stream switcher

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.

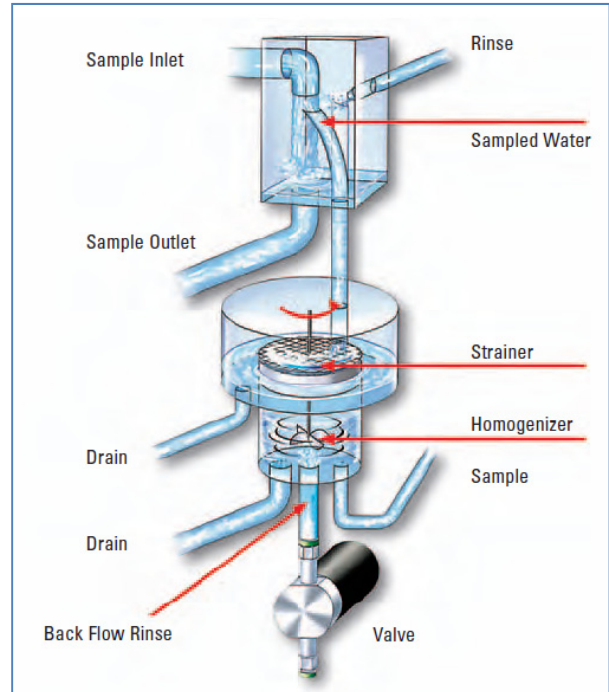


Fig.: Multi-stream suspended solids pretreatment unit

### ■ 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 ( $\text{pH} \geq 12$ ) 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.

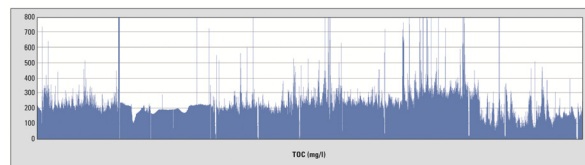


Fig. Diagram of 27.000 Measurement results (three months)

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 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.

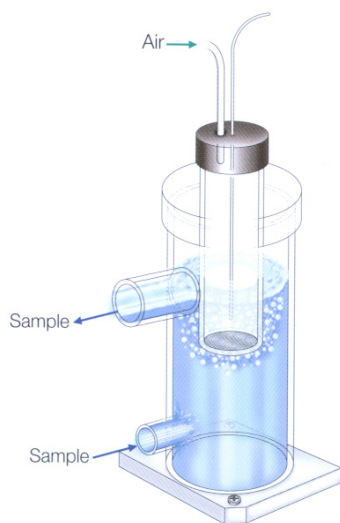


Fig. Sampling

### ■ TOC measuring method

TOC determination is often carried out via the NPOC method,

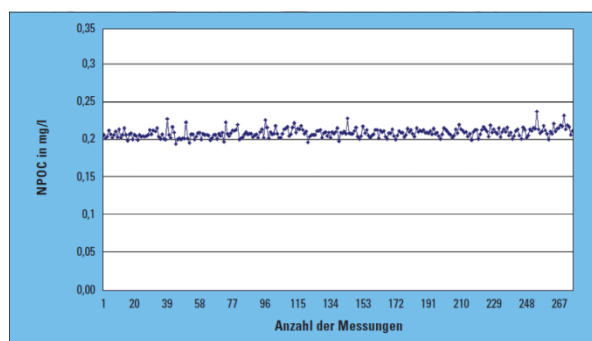
whereby the inorganic carbon content (carbonates and hydrogen carbonates) is removed prior to the actual analysis. For this purpose, the sample is drawn from the continuous sample stream into a syringe and automatically acidified via the 8-port valve (pH 2).

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

Founded in 1875, Shimadzu Corporation, a leader in the development of advanced technologies, has a distinguished history of innovation built on the foundation of contributing to society through science and technology. We maintain a global network of sales, service, technical support and applications centers on six continents, and have established long-term relationships with a host of highly trained distributors located in over 100 countries.

For information about Shimadzu, and to contact your local office, please visit our Web site at [www.shimadzu.eu](http://www.shimadzu.eu)



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