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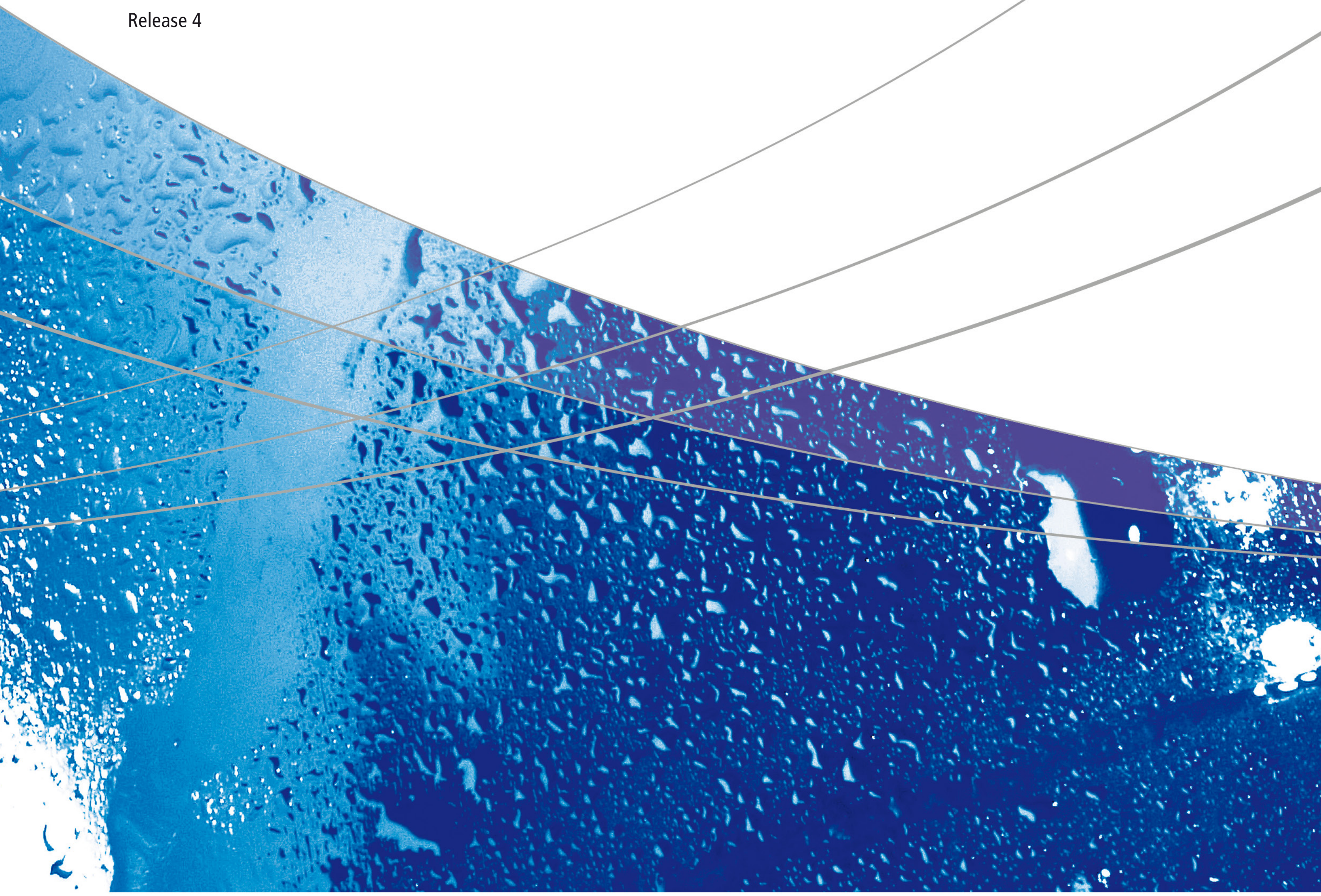
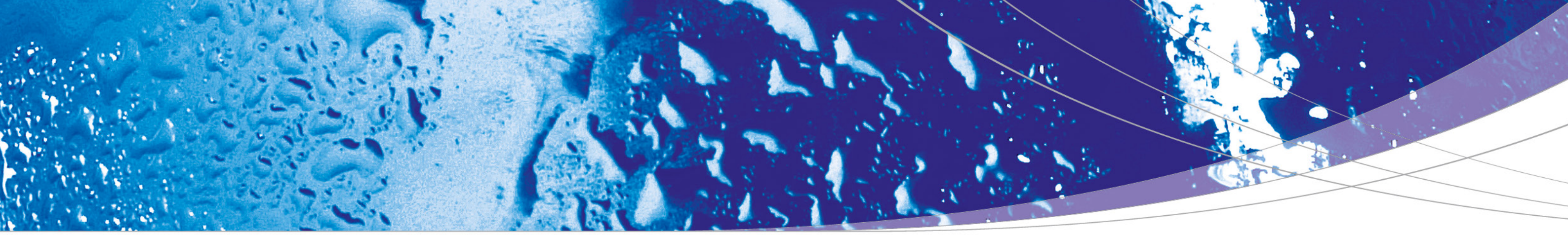
SEG-A-099

Application Handbook

Sum Parameter

Release 4





Content

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1. Environmental analysis

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 abovementioned 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 Stowing 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.’

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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 mg/l (RSD = 2%) ± 2 mg/l
(98 – 102 mg/l)

IC = 98 mg/l (RSD = 2%) ± 1,96 mg/l
(96,04 – 99,96mg/l)

Based on error propagation the total error is ± 3,96 mg/l

TOC (calc.) = 2 mg/l ± 3,96mg/l
(- 1,96 - 5,96 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.

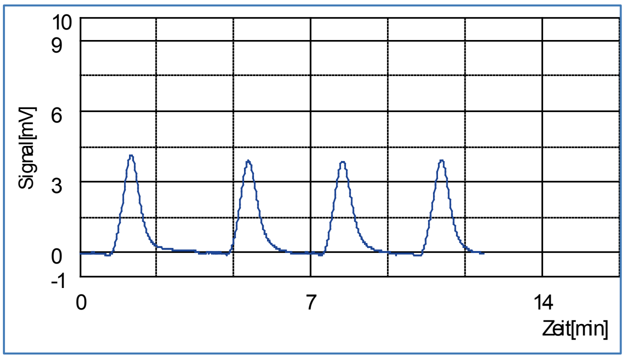
The ISP (integrated sample preparation) module consists of an 8-port valve and a syringe with sparging gas connection. In addition to acidification and sparging in the syringe, the ISP also enables automatic dilution. This feature facilitates an extended measuring range, dilution of highly contaminated 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 $_{CPH}$

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

TOC-V_{WP} 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

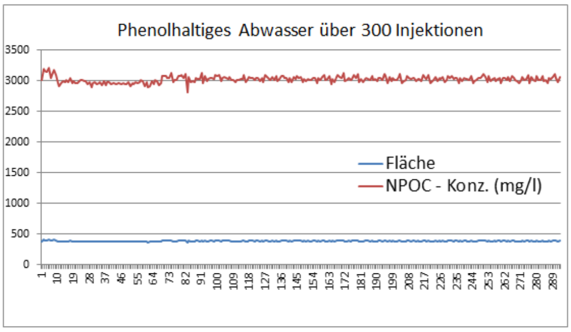
2) the run-off and collected water (rainwater) from built-up or paved areas following precipitation.

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_{CPN} 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 in homogeneity 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 $_{CPN}$ 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)

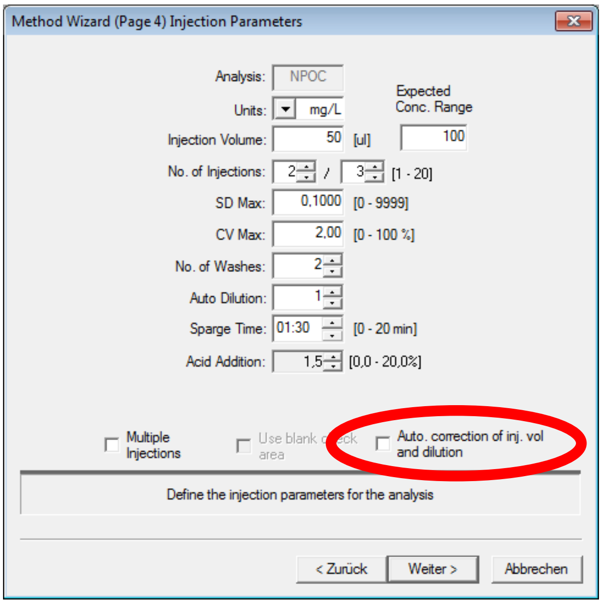
Depending on the region, high TIC concentration (> 100 mg/L) can also occur in surface water as well as in groundwater.

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

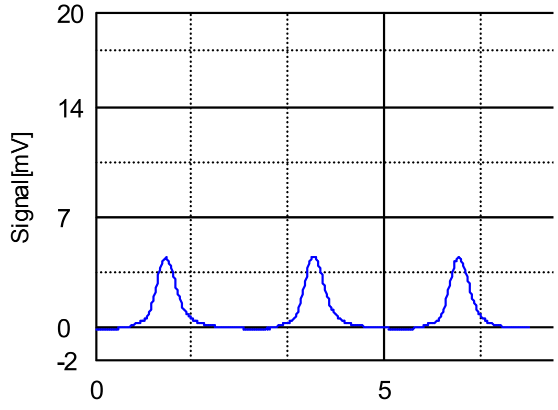
■ **TOC-L**

To prepare the sample accordingly, the ISP module of the TOC-L automatically acidifies the sample and strips the CO_2 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%
Sparge-time: 5 Minutes

TOC-Concentration: 3,4 mg/l
RSD (3 Injections): 1,4%

■ **Recommended analyzer / Configuration**

- TOC-L$_{CPH}$

- ASI-L (40ml) with stirrer option
- External Sparge-Kit

(1) Source: Wikipedia

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Sum parameter – Total Organic Carbon

TOC – Determination in seawater

No. SCA-130-104

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.

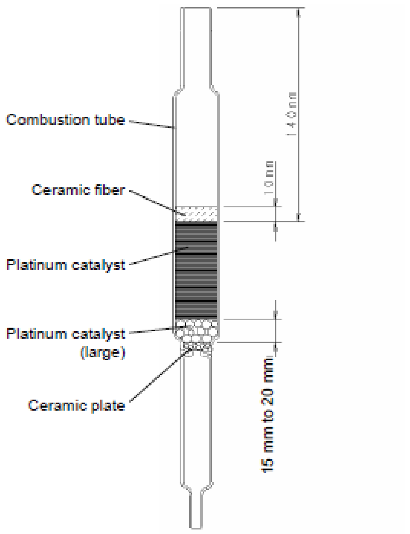
■ TOC-L Series

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_2.

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 $NaSO_4$ 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_2SO_4	888°C
$MgCl_2$	708°C
$CaCl_2$	782°C
K_2SO_4	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.

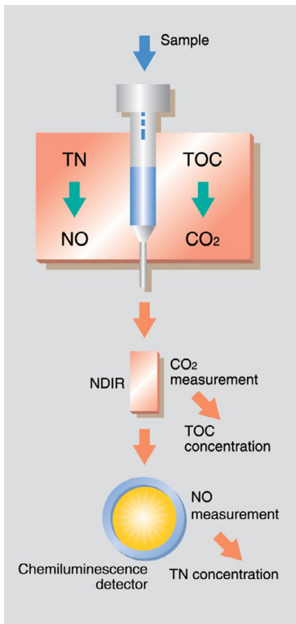


Figure: Simultaneous TOC/TN-Determination

■ Recommended analyzer / Configuration

TOC-L $_{CPN}$
ASI-L (40ml), External Sparge-Kit.
Kit for high-salt samples
TNM-L

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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 (Abfallablagerungsverordnung, AbfAblV), 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_2 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).

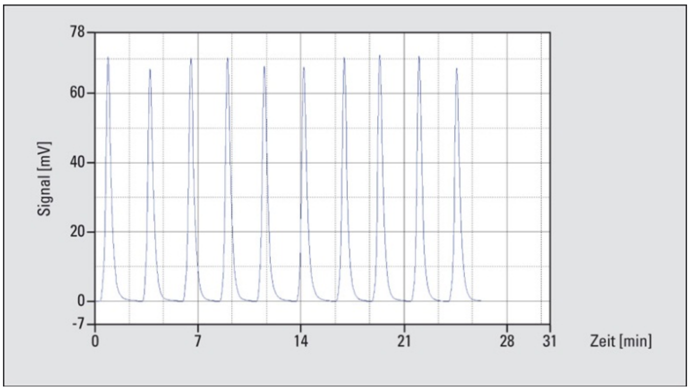
■ Analytical process

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
MW	**182,2**	**24,5**	**2,45**
RSD in%	**1,88**	**2,52**	**2,49**

■Recommended analyzer / Configuration

TOC-L $_{CPN}$
ASI-L (40ml) with stirrer option and external Sparge-Kit.

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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 tosediment 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$_{CPH}$ 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$_{CPH}$ was first calibrated using the automated dilution function in the range of 10 – 100 mg/L.

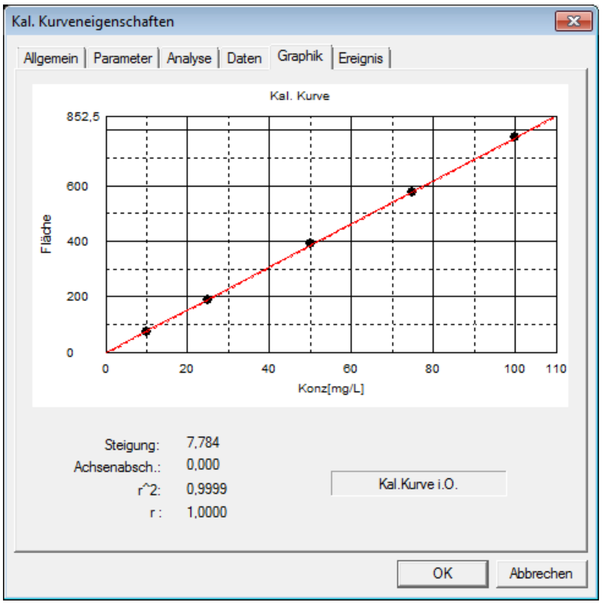

Figure 1 Calibration curve 10-100mg/L

■ Settings

- Injection volume 90 µL
- 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: 20-100µm
Supplier: Machery-Nagel

■ Results

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

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

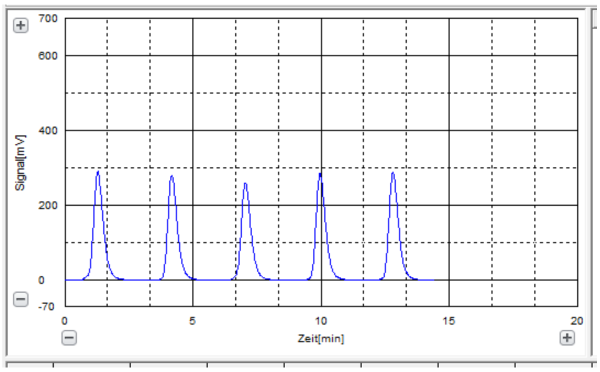

Abb.2 Peak graph of cellulose-suspension

These values are clearly within EN DIN specifications

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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 10th 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.

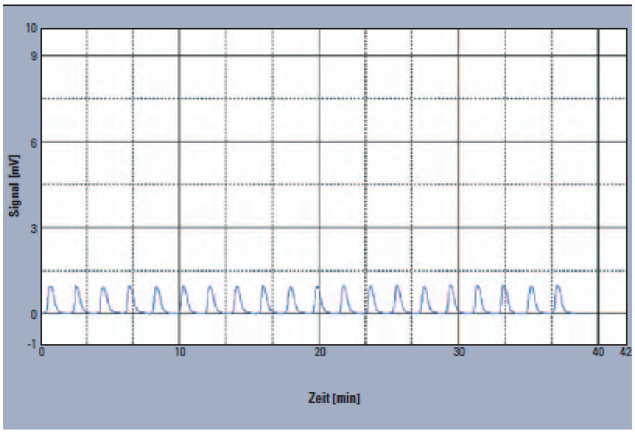

Fig. Peak graphs of the last 20 injections

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
Mean Value	0,6945
SD	0,0124
RSD in %	1,78

Tab. Peak areas and statistics of the last 20 injections

■ Recommended analyzer / Configuration

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

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Application News

No. SCA-130-108

Sum parameter – Total Organic Carbon

TOC determination in soils, sludges and sediments using the solid sample module

To characterize soils, sludges or sediments, the total organic carbon parameter (TOC) is regularly used. In addition to naturally occurring organic components in these solids, undesirable organic contaminations caused by man and industry are also often present. These organic compounds frequently are risks. Solids to be disposed or utilized must be tested on their TOC content. The organic contaminations can contaminate ground water, for instance when leached out. In addition, hazardous gases such as methane can be formed through biological activities in the soil and compromise the safety of landfills. The formation of such gases or the biological decomposition of organic materials in soils, inevitably lead to the formation of cavities that reduce the stability of the materials and renders them unsuitable for specific application areas, such as road construction.

This is why different TOC limit values are specified for soil replacement and for deposits in landfills.

■ TOC determination

To investigate the TOC in soils or other solids such as sediments or sludges, a solid sample module is used which enables TOC determination using the difference method and the NPOC method.

Here, a subsample of the dried solids is weighed into a ceramic boat and combusted at 900 °C in a stream of oxygen. To ensure complete conversion to CO_2, the generated gases are passed over a mixed catalyst (cobalt/platinum) for catalytic post-combustion.

The determination of the inorganic carbon is carried out in a separate furnace of the module. Phosphoric acid is added to the sample and the resulting CO_2 is purged at 200 °C and measured.

The SSM-5000A solid sample module does not have its own detector, but is coupled to the NDIR detector of the main instrument (TOC-V or TOC-L). The detector is equipped with two coupled measuring cells that way to complete the measurement of solids and liquids consecutively without any additional conversion.

The module is fully integrated into the TOC-Control software which automatically calculates the TOC-content.

■ NPOC determination

For the NPOC method, the sample is acidified in order for the CO_2 to be purged from the carbonates and hydrogen carbonates. This pretreated sample is then used to determine the TC (and thus the NPOC).

■ Additives

Large amounts of earth-alkali compounds such as barium or calcium carbonate can be difficult to determinate. Bicarbonate, for instance, needs temperatures up to 1200°C to be thermally decomposed.

Small amounts of additives such as vanadium (V) oxide or tungsten oxide are added to such samples. They act as catalysts and ensure complete determination.

■ Calibration

Calibration can be performed in different ways. Usually, the calibration is carried out in the solid sample module using different sample weights of a solid with known carbon content, for instance glucose which contains 40% carbon. For the different sample weights (in µg absolute carbon), the absolute amount of carbon is plotted on the X-axis of the calibration graph.

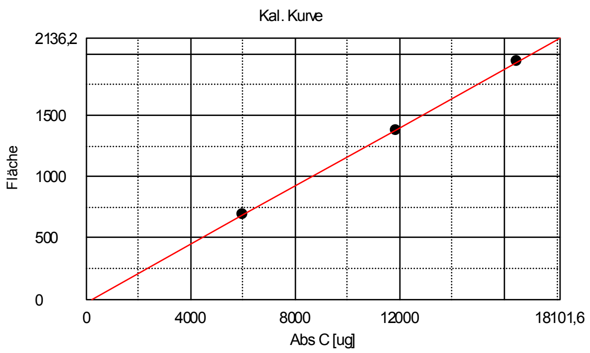


Abb.: TOC calibration in the SSM-5000A using Glucose.

Calibration of the IC is carried out in the same way, for instance using sodium hydrogen carbonate.

■ Detection limit

The detection limit for this method is at 0.1 mg C. For a soil sample weight of 1 g, a theoretical detection limit of 0.01 wt.% TOC is obtained.

■ Example of a solid sample measurement

Sample type: contaminated soil

Sample weight: 1st Peak: 110 mg
2nd Peak: 190 mg

Result: 1.) 4.04 % TC
2.) 4.08 % TC

Mean value: 4.06% TC

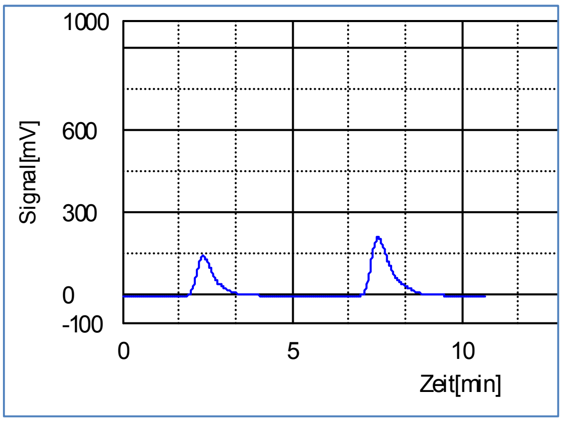


Abb.: Peaks for various sample weights.

■ Recommended instrument / equipment

TOC-L_{CXX}
TOC-V_{WX}
SSM-5000A

Application News

No. SCA-130-109

Sum parameter – Total Organic Carbon

Determination of microbial biomass in soils - TOC in soil science

Fertile soils contain a multitude of micro-organisms. They are responsible for the degradation of organic substances and protection of the nutrient cycle. To evaluate soils in terms of their biodegradability and their fertility, the microbial biomass of the soil, i.e. the organic carbon fraction that is bound to these tiniest organisms, is determined.

The fumigation-extraction method is a commonly used method for the determination of microbial biomass in soils. The microbial biomass is described regarding extractable organic carbon compounds before and after killing off the microorganisms.

In the fumigation-extraction method, a subsample of the soil is treated with chloroform gas in a suitable apparatus (e.g. a desiccator) over an extended period of time of at least 24 hours. This destroys the cell walls and kills off the microorganisms. After fumigation, the chloroform remaining in the soil is removed.

■ DOC – Determination

Subsequent to fumigation, each fumigated subsample and one non-fumigated soil sample is mixed with a 0.5 M (mol/L) potassium sulfate solution and then shaken. After filtration of the eluate, the DOC (dissolved organic carbon) of the extracts is determined. Since experience has shown, not all cells are destroyed and extracted, and an empirical correction factor is additionally applied. (An exact description of the fumigation-extraction method is found in the EN ISO 14240-2:2011 standard).

■ Kit for high salt loads

The kit for high salt loads was used for these measurement because the extraction solution alone has a salt load of approximately 87 g/L. High salt loads can lead to clogging of the catalysts and the combustion tube. This special kit consists of a combustion tube featuring a specific geometry and a unique catalyst mixture. This particular catalyst can handle up to 12 times more salt than a conventional catalyst.

■ Long-term test with 600 injections

A long-term test should show that an application, such as the analysis of soil extracts from a 0.5 M potassium sulfate solution can be carried out problem-free using a kit for high salt load samples. For this test, a 0.5 M K_2SO_4 solution (corresponding to 87 g/L) was injected 600 times onto the kit for high-salt samples.

■ Method parameter

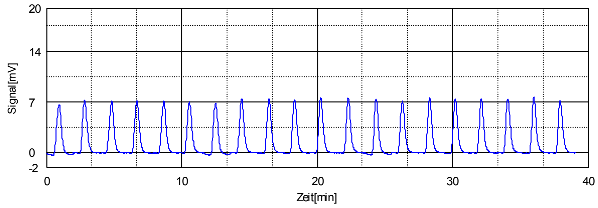
NPOC preparation: automated
Acidification: 2%
Sparging: 6 Minutes
Injection volume: 50 µl
Calibration: 0,5 mg/l to 10 mg/l.

■ Results

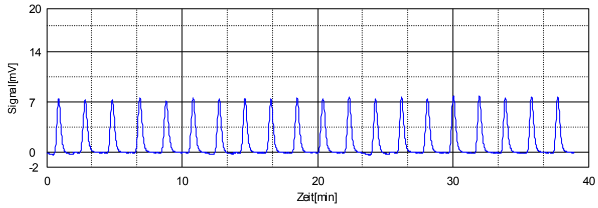
	Area	NPOC-concentration [mg/l]
Mean value	17,01	6,66
Standard deviation	0,392	0,153
Standard deviation in %	2,3	2,3

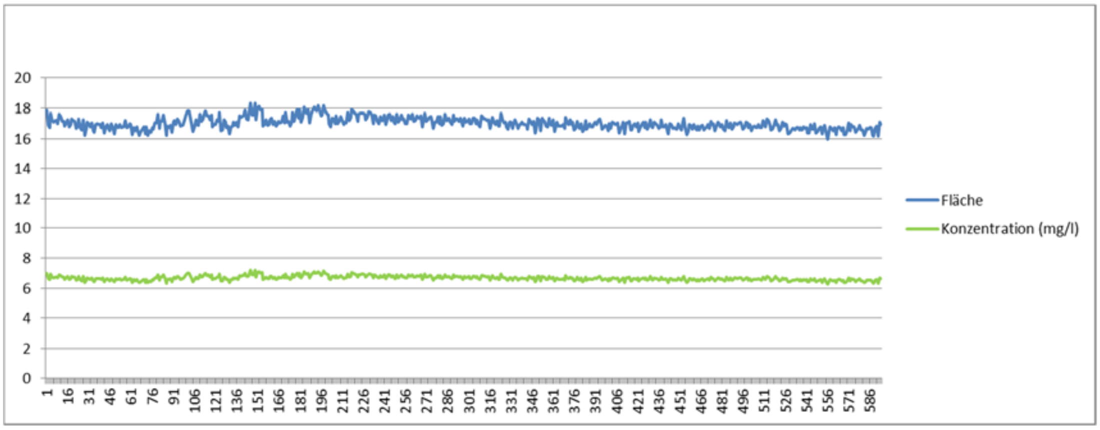
Even after 600 injections, the peak shapes remain exactly the same as at the start of the injection series.

Here in comparison the peak graphic of injection 1-20



and the peak graphic of injection 581-600





Sequence (area and concentration) of the 600 injections

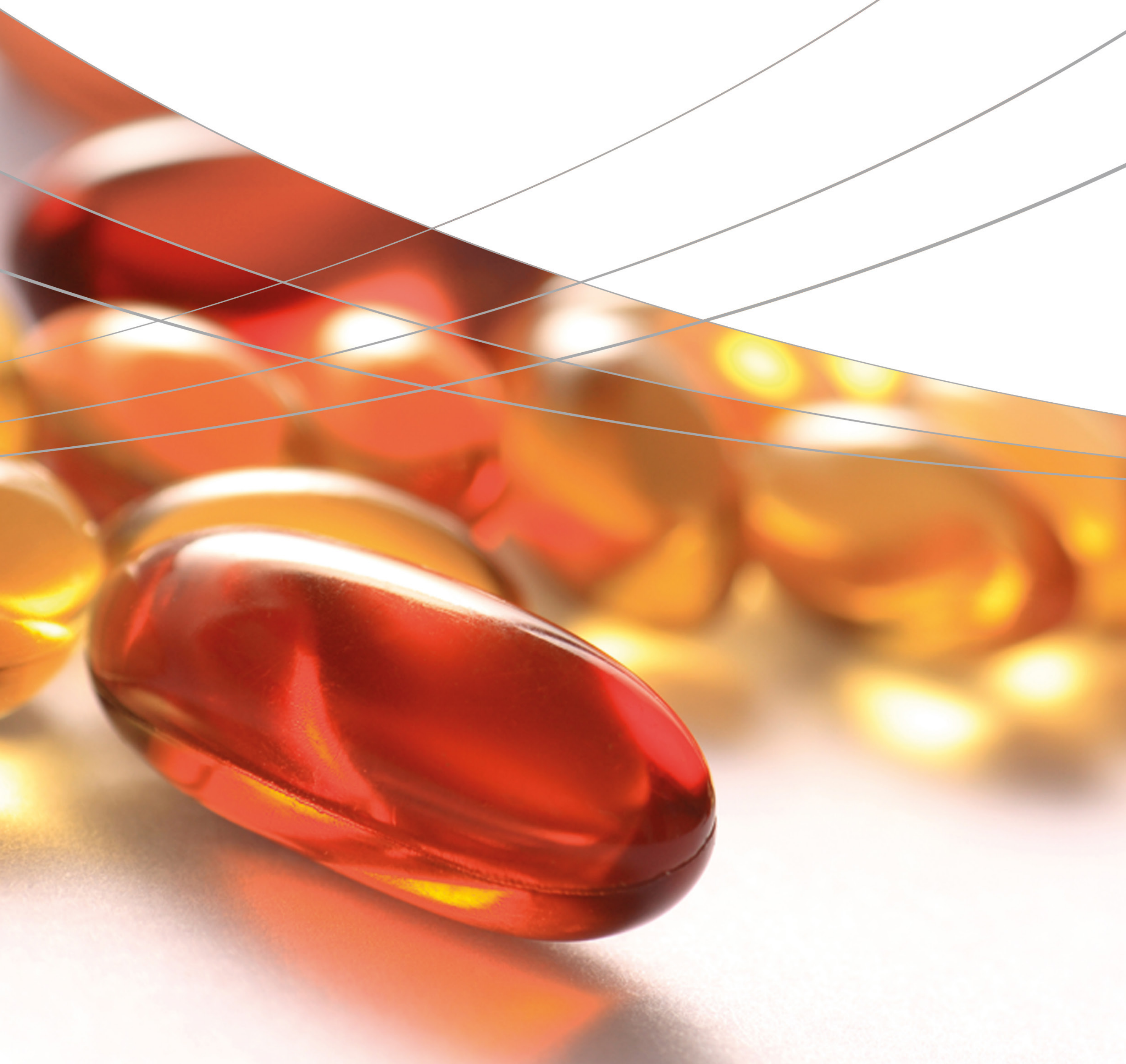
■ Conclusion

As one can see, the TOC-L in combination with the kit for high salt load samples is highly suitable for TOC determination of salt-containing samples, such as soil extracts from a 0.5 M potassium sulfate solution.

■ Recommended Analyser / Configuration

TOC-LCXX
Kit for high salt loads

2. Pharmaceutical industry



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 accordance 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.’

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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.

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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_2 using a catalyst under high temperatures with subsequent detection of the resulting CO_2 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$_{CPH}$: Oxidation via catalytic combustion

The TOC-L $_{CPH}$ 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.

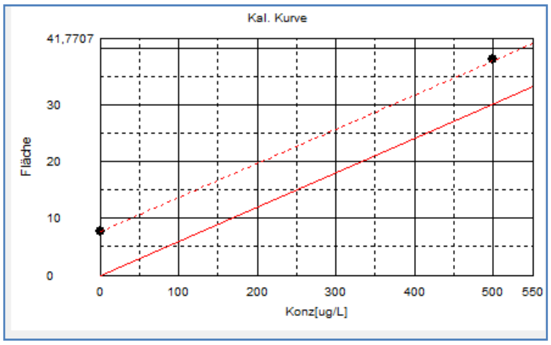

Fig. NPOC- Calibration (Blank and 500µg/L)

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_b determination is highly suitable for cleaning validation, as this enables differential determination between cleaning agent and product.

■ TOC-$V_{WP/WS}$: Wet chemical oxidation

The key technique of the TOC-$V_{WP/WS}$ analyzer is the powerful oxidation via the combination of sodium persulfate and UV oxidation at 80 °C. The TOC-$V_{WP/WS}$ 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-$V_{WP/WS}$ 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)

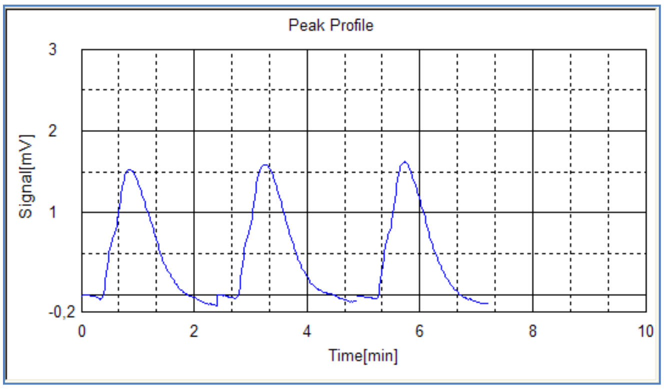

Abb. Peak graphik of TOC-V_{WP} measurement

■ 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/TNb 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_{CPH} with high sensitivity catalyst
ASI-L (40ml), External Sparge-Kit.

TOC-V_{WP} with ASI-V (40ml)

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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_2 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$_{CPH}$ 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.

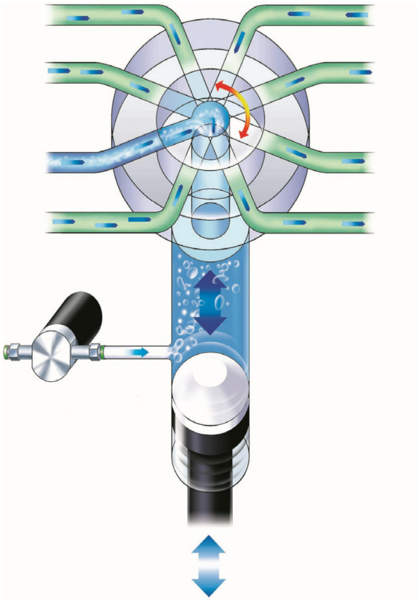


Fig. ISP-Module of TOC-L series

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$_{WP}$ analyzer with its various options, is available. The key technique of the TOC-V$_{WP}$ 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$_{CPH}$
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_2. To ensure complete oxidation, there is an additional catalyst in the combustion tube. The resulting CO_2 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.

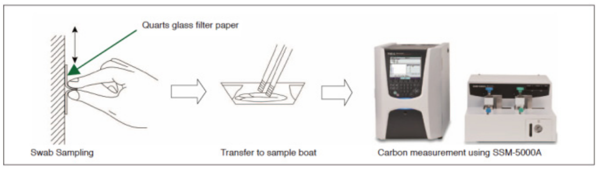
■ Preparation

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 wiht 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

No. SCA-130-204

Sum parameter – Total Organic Carbon

TOC-Determination according to EP 2.2.44

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 Pharmacopeia

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.

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.

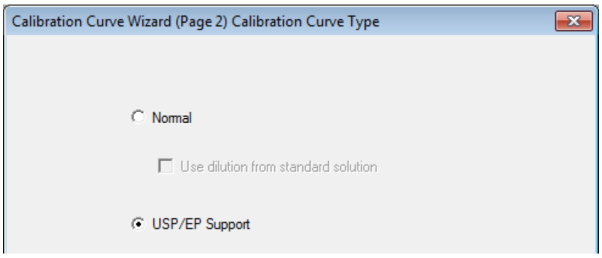


Fig. Calibration curve wizard

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

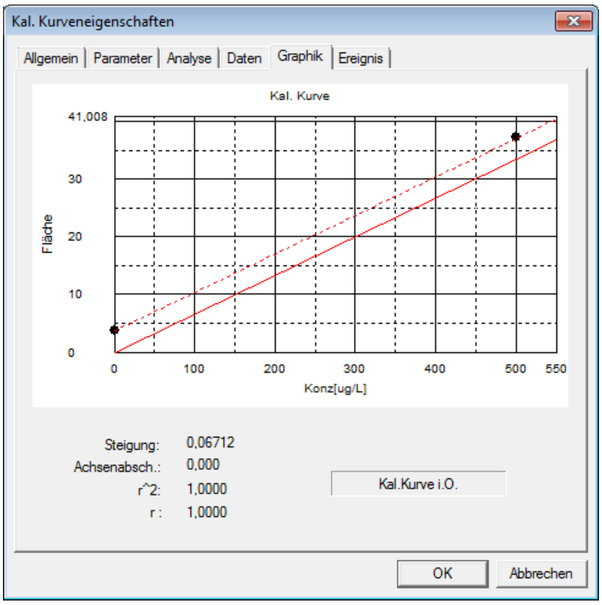


Fig. Calibration Curve

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

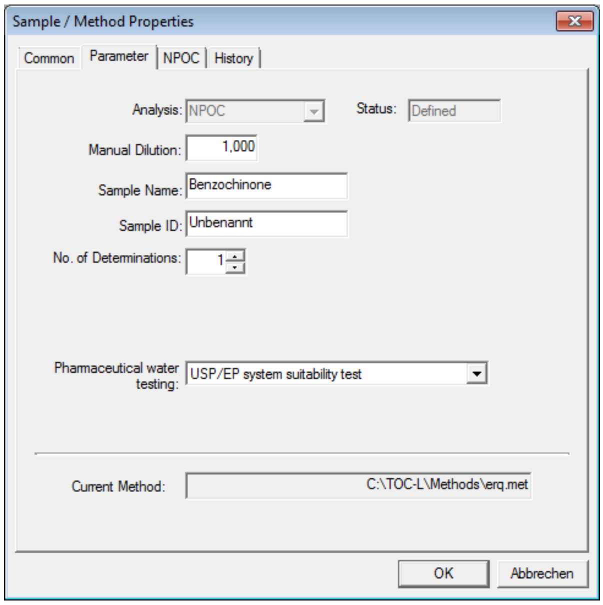
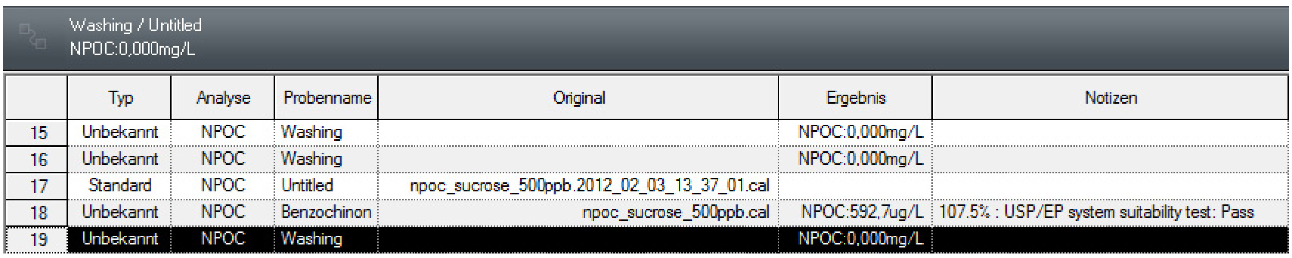


Fig. Benzochinone-Determination

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).



	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

Application News

Sum parameter – Total Organic Carbon

TOC determination in ultra pure water with wet chemical oxidation

No. SCA-130-205

The quality of ultra pure water is of crucial significance in a large number of application areas such as monitoring of water quality in water treatment plants, and in industries such as chip manufacture or pharmaceutical production. Determination of Total Organic Carbon (TOC) is playing an increasingly important role in quality control.

The TOC value indicates whether ultra pure water still contains any organic contaminants. TOC determination is fast and accurate and is defined in the European Pharmacopoeia (EP) as a control parameter for WFI-water (water for injection).

■ TOC determination in ultra pure water

Two oxidation techniques are now commonly used in TOC analysis: catalytic combustion and wet-chemical oxidation. In catalytic combustion, carbon compounds are converted to CO_2 using high temperatures and a catalyst, with subsequent detection of the resulting CO_2 using an NDIR detector. Wet-chemical oxidation uses a combination of UV irradiation and persulfate oxidation. Both methods are suitable for TOC determination in ultrapure water.

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

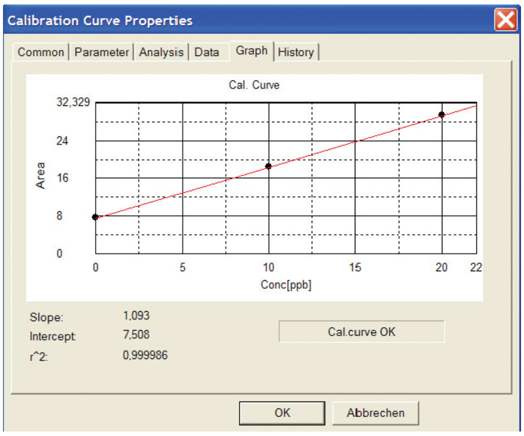
■ TOC-V WP with wet chemical oxidation

The fundamental technique of the TOC-V WP/WS analyser is powerful oxidation via the combination of sodium persulphate and UV oxidation at 80 °C. These features guarantee that all dissolved carbon species will be detected. An automatic reagent preparation function eliminates possible contamination of the reagent solution and minimizes the blank value of the instrument. These features, together with the high injection volume (up to 20.4 mL) and the highly sensitive NDIR detector, result in extremely low detection limits and excellent reproducibilities in the low ppb-range.

This is why the TOC-$V_{WP/WS}$ is especially suitable for TOC determination in the ultra-trace range.

■ Calibration:

Method:	NPOC
Acidification:	3%
Sparge time:	3 minutes
Oxidizer:	1,5%
Injection volume:	20,4 ml



Data according to DIN 32645

Limit of detection: 0,3µg/l TOC (NPOC)

Limit of quantification: 2,2µg/l TOC (NPOC)

■ TOC-Control V Software

In the pharmaceutical industry TOC systems are used in a regulated laboratory environment and therefore these systems are subject to various regulations that particularly apply to instrument software.

The TOC-Control V software running the TOC-V series provides full support for complying with the regulations, while still remaining extremely user-friendly.

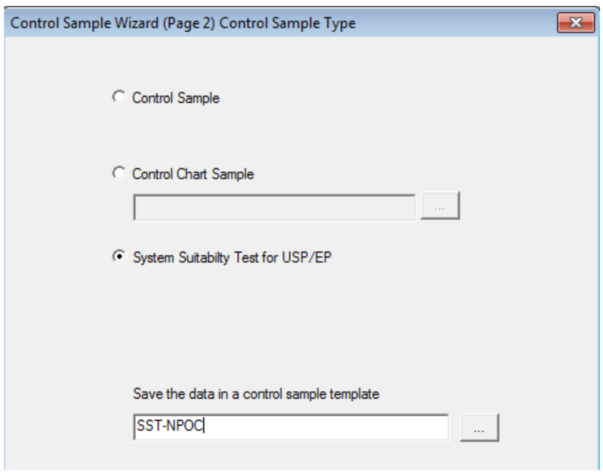
Already during software installation, the operating criteria of the software are decided. The selected parameters cannot be deactivated later.

The software use is enabled via user access rights. It offers user accounts on four different levels, each protected through own passwords. The administrator can individually change access rights for each user. The software allows changing of login during ongoing operation. This is especially important for laboratories working under multiple shift operation

All software operations are stored automatically in the audit trail. This happens entirely in the background. Only when existing parameters are changed is a user comment required. Data storage takes place in an MSDE database.

The TOC-Control V 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.

The system suitability test is defined in a special control sample template. Subsequent to the measurement of the control sample (benzoquinone), the recovery is calculated automatically, compared with the predetermined limits (85 – 115 %) and documented.



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Application News

No. SCA-130-206

Sum parameter – Total Organic Carbon

TOC – Determination according to USP 643 (USP 36-NF 31)

In 1996, the US Pharmacopeia has introduced the TOC parameter for the determination of impurities in purified water and water for injections. For other waters used in the pharmaceutical industry, the wet-chemical potassium permanganate test continued to be used. Meanwhile however, TOC determination has proven to be so effective that it now replaces the wet-chemical test.

In the current version of the UPS <643> (USP 36-NF 31) a distinction is made between 'bulk water' and 'sterile water'. The chapter 'Bulk Water' includes purified waters that are to be used right away as purified water, water for injection, water for hemodialysis and as condensate of pure steam. The following known conditions apply to TOC determinations:

Limit of detection:	< 0.05 mg/L C
Blank water, r_w:	max. 0.1 mg/L C
Standard (sucrose), r_s:	0.5 mg/L C
SST (benzoquinone), r_{ss}:	0.5 mg/L C
Permitted response:	85 – 115%
Limit response (waters) r_u:	< (r_s-r_w)

The chapter 'Sterile Water' is new. It includes sterile purified water, sterile water for injections, sterile water for irrigation and sterile water for inhalation. Sterile water can be stored in various packaging configurations. In comparison to bulk water, however, other conditions for TOC determination apply:

Limit of detection:	< 0.05 mg/L C
Blank water, r_w:	max. 0.1 mg/L C
Standard (sucrose), r_s:	8 mg/L C
SST (benzoquinone), r_{ss}:	8 mg/L C
Permitted response:	85 – 115%
Limit response (waters) r_u:	< (r_s-r_w)

■ Impact of the new determination

The present requirements of the UPS <643> (bulk water) are consistent with the requirements of the European Pharmacopeia (limit of detection, concentration of the standard solution (sucrose) and system suitability solution (benzoquinone and response). Validation of the TOC system for both determinations is therefore sufficient.

In accordance with the new USP <643>, the implementation of a system suitability test using higher concentrations is required.

For users of Shimadzu's TOC systems, this just means the creation of an additional calibration curve (sucrose, 8 mg/L, see figure 1) and control sample (benzoquinone, 8 mg/L, see figure 2) as well as extension of the current validation process with these data.

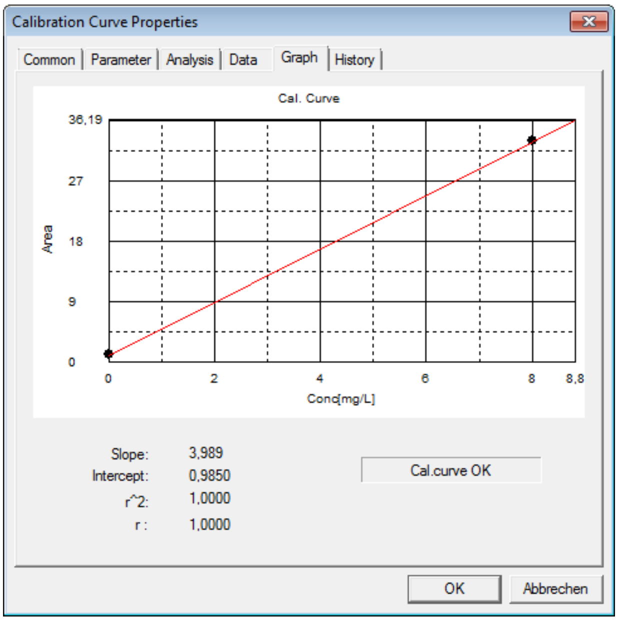


Figure.1 : Calibration Curve, Sucrose 8mg/L

Additional modifications of the TOC system are not necessary.

■ Shimadzu TOC-System

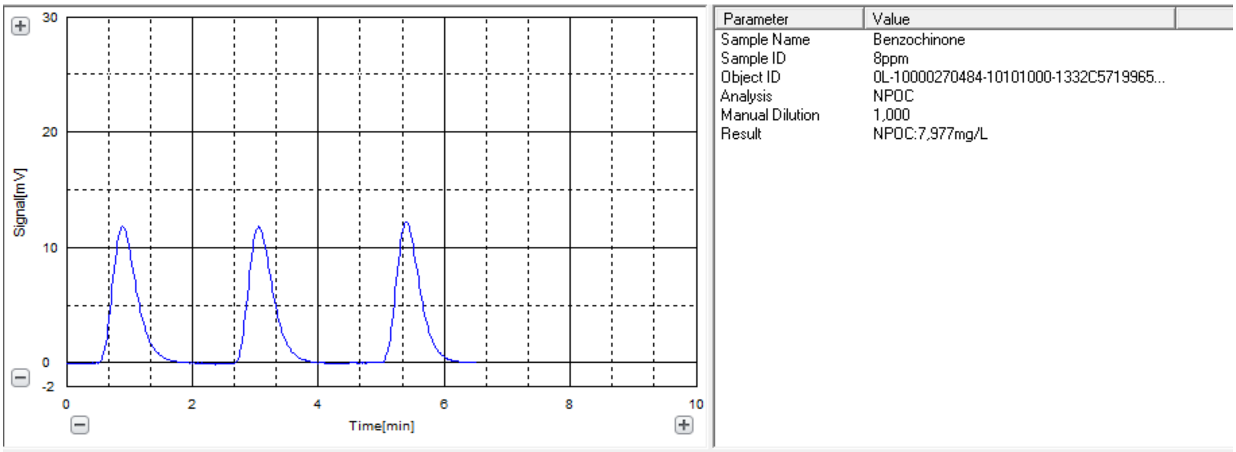
Shimadzu offers two systems that are ideally suitable for TOC determination in ultrapure water. The TOC-VWP/WS uses wet-chemical oxidation, whereas the TOC-LCPH uses catalytic combustion at 680 °C. With their wide measuring range of 0.5 µg/L up to 30,000 mg/L, the instruments support any application – from ultrapure water (for instance in cleaning validation) to highly polluted waters (such as wastewaters). Shimadzu TOC-Systems.

Both types of instrument with their different oxidation methods can be used for TOC determination in accordance with the new United States Pharmacopeia (USP <643>) and the European Pharmacopeia (EP 2.2.44). The advantage of the combustion method is its high oxidation potential, especially for samples containing particulate matter. Moreover, simultaneous TOC/TN_b measurements can be carried out, leading to a higher information content of the analysis. The advantage of wet-chemical oxidation is its very high injection volume, which leads to higher sensitivity and therefore enables high precision measurements in the lower ppb range.

■ Recommended Analyser / Configuration

TOC-L $_{CPH}$ with high sensitive catalyst
ASI-L (40ml), external sparge kit

TOC-V_{WP}
ASI-V (40ml), external sparge kit



	Spl. No.	Inj. No.	Area	Mean Area	Conc.	Result	SD Area	CV Area	Inj. Vol.	Calibr. Curve	Date / Time
	1	1	32,73	32,81	7,957	NPOC:7,977	0,1779	0,54	51	npoc_sucrose_8ppm.2013_0	03.09.2013 12:
		2	33,01		8,028				51	npoc_sucrose_8ppm.2013_0	03.09.2013 12:
		3	32,68		7,945				51	npoc_sucrose_8ppm.2013_0	03.09.2013 12:

Figure. 2: SST, Benzochinone 8mg/L

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Application News

No. SCA-130-207

Sum parameter – Total Organic Carbon

TOC – Determination according to USP 661.1 Testing of Plastic Packaging Systems and their Materials of Construction

Plastic packaging systems for pharmaceutical products must be suitable for their intended use. The US Pharmacopeia revised the related chapter. It is published in USP 39-NF34, which will be valid from May 2016.

Besides to the change of the title "Plastic Packaging Systems and their materials of Construction", two new chapters are established.

This application note is related to the first chapter 661.1.

■ 661.1 Plastic Materials of Construction

The purpose of this chapter is to provide test methods and standards for plastic materials (e.g polyethylene, polyolefins, polypropylene) of construction used in packaging systems for therapeutic products. The characterization is done by identity, biocompatibility (biological reactivity), General physicochemical properties and Additives and extractable metals.

The TOC parameter as an indicator for extractable material is part of the physiochemical properties that must be determined.

For the TOC determination a purified water extraction is prepared. For example 25g plastic material is placed in a glass flask, 500ml purified water added and boil under reflux condition for 5h. After cooling, the solution is pass through a sintered-glass filter. The parameter of the sample weight, purified water volume and heating temperature and time depends of the used plastic sample.
The TOC of the ultra-pure water is subtracted for the measured value of the extraction solution. The resultant TOC value must not exceed 5mg/l.

■ TOC determination in pharmaceutical application

The TOC determination is performed according to the USP<643>. This regulation describes the TOC determination for pure water, purified water and water for injection. It does 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.
However, material extracts may have TOC values that are higher than those of purified water because of extracted organic substances.
Thus the TOC analyses performed should have a limit of detection of 0,2mg/L and should have a demonstrated linear dynamic range from 0,2 – 20mg/L.

■ **Shimadzu TOC-System**

Shimadzu offers two systems that are ideally suitable for TOC determination in ultrapure water. The TOC-VWP/WS uses wet-chemical oxidation, whereas the TOC-LCPH uses catalytic combustion at 680 °C.

Both types of instrument with their different oxidation methods can be used for TOC determination in accordance with the United States Pharmacopeia (USP <643>) and the European Pharmacopeia (EP 2.2.44).

■ **Linear dynamic range from 0,2 – 20mg/L**

To prove the required dynamic range, a calibration with TOC-L CPH (with high sensitivity catalyst) was carried out in a range of 1,0 mg/L – 20mg/L.

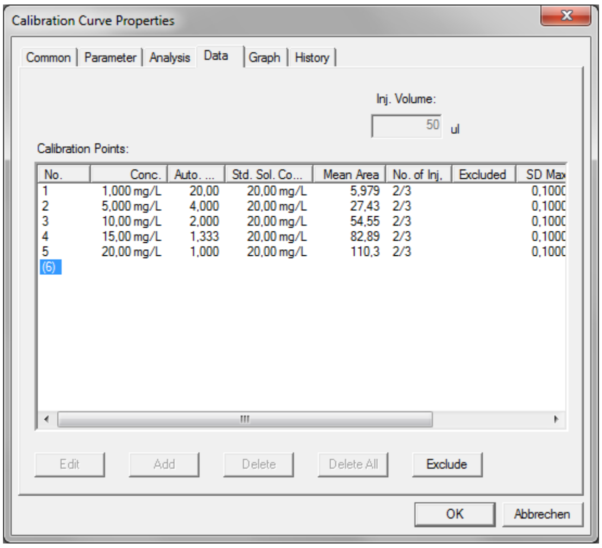

Figure.1 : Calibration Curve 20mg/L, results

For the dilutions, the automatic dilution function of the TOC-L system was applied.

The injection volume is determined, based on the highest calibration standard. For 20mg/L the default injection volume is 50µl.

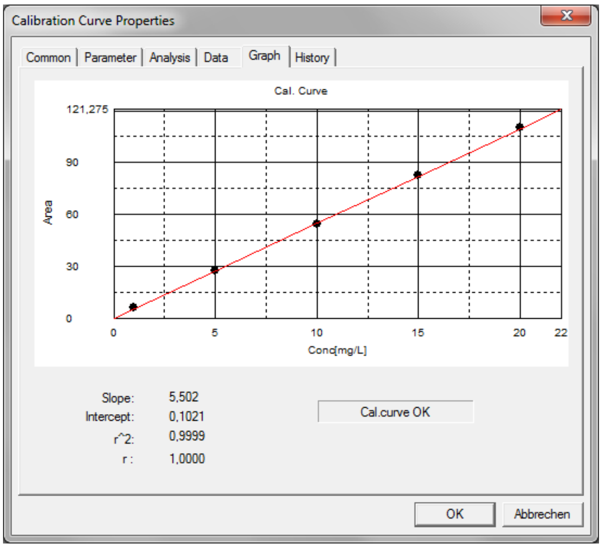

Figure.2 : Calibration Curve 20mg/L, graphic

The calculation of the limit of detection limit according to DIN 32645:

Characteristics

Slope a:	5,503
Intercept b:	0,091
Correlation coefficient r:	0,9999
Result uncertainty:	33,3%
Probability of error (a):	5,00%
Number of injections:	2

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Limit of detection: 0,2mg/L

These results show that the TOC-CPH with high sensitivity catalyst covers the required linear dynamic range from 0,2 – 20mg/L. This means both applications, purified water and this extraction solution can be measured with a single TOC-L CPH instrument.

■ **Recommended Analyzer / Configuration**

TOC-L $_{CPH}$ with high sensitive catalyst

ASI-L (40ml), external sparge kit

■ **Source**: www.usp.org

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Shimadzu Europa GmbH

www.shimadzu.eu

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Application News

No. SCA-130-208

Sum parameter – Total Organic Carbon

TOC – Determination according to USP 661.2 Testing of Plastic Packaging Systems and their Materials of Construction

In the pharmaceutical industry plastic packaging is used in various forms – for example for intravenous bags, bottles, cartridges or pre-filled syringes. The packaging must be tested for suitability for these uses. It is published in USP 39-NF34, which will be valid from May 2016.

Besides to the change of the title “Plastic Packaging Systems and their materials of Construction”, two new chapters are established.

This application note is related to the second chapter 661.2.

■ 661.2 Plastic packaging system

This chapter deals with the required testing of the final packaging system since packaging often consists of than one plastic material. Characterization takes place by identifying and determining the biocompatibility, general physicochemical properties and Additives.

The TOC Parameter as an indicator for extractable organic material is part of the physio-chemical characteristics that must be determined.
For testing the packaging system, it is filled with ultra-pure water, sealed and heated in an autoclave. The temperature and dwell time depend in the plastic used. In order to determine the blank value, ultra-pure water is poured into a glass flask and heated to the same temperature. The TOC of both solutions is determined. The difference between the two measured TOC values should not exceed 8mg/L.

■ TOC determination in pharmaceutical application

The TOC determination is performed according to the USP<643>. This regulation describes the TOC determination for pure water, purified water and water for injection. It does 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.
However, material extracts may have TOC values that are higher than those of purified water because of extracted organic substances.
Thus the TOC analyses performed should have a limit of detection of 0,2mg/L and should have a demonstrated linear dynamic range from 0,2 – 20mg/L.

■ Shimadzu TOC-System

Shimadzu offers two systems that are ideally suitable for TOC determination in ultrapure water. The TOC-VWP/WS uses wet-chemical oxidation, whereas the TOC-LCPH uses catalytic combustion at 680 °C.
Both types of instrument with their different oxidation methods can be used for TOC determination in accordance with the United States Pharmacopeia (USP <643>) and the European Pharmacopeia (EP 2.2.44).

■ Linear dynamic range from 0,2 – 20mg/L

To prove the required dynamic range, a calibration with TOC-L CPH (with high sensitivity catalyst) was carried out in a range of 1,0 mg/L – 20mg/L.

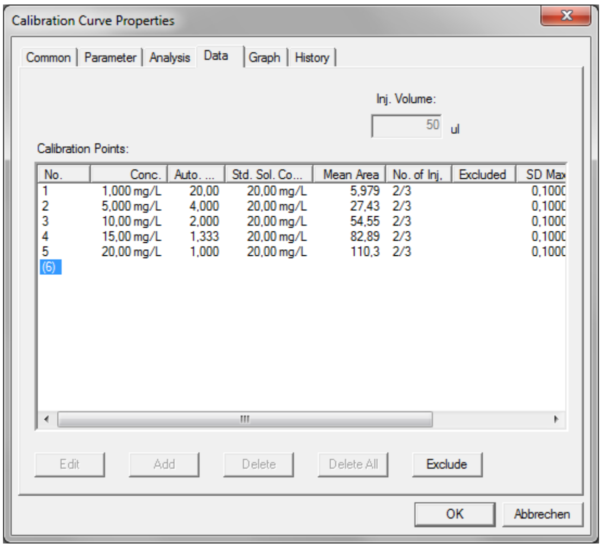

Figure.1 : Calibration Curve 20mg/L, results

For the dilutions, the automatic dilution function of the TOC-L system was applied. The injection volume is determined, based on the highest calibration standard. For 20mg/L the default injection volume is 50µl.

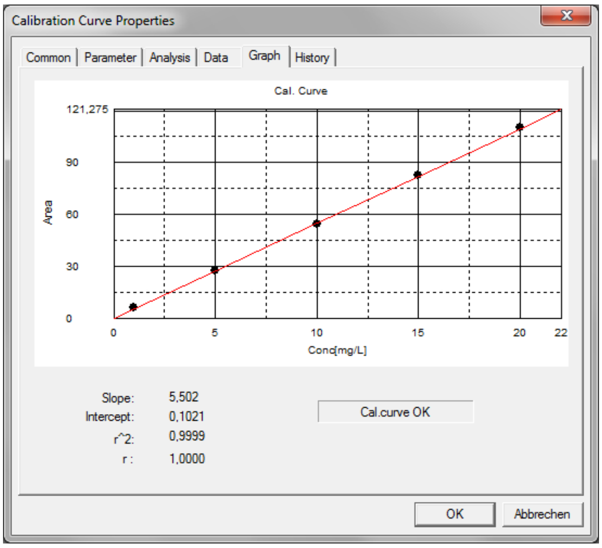

Figure.2 : Calibration Curve 20mg/L, graphic

The calculation of the limit of detection limit according to DIN 32645:

Characteristics

Slope a:	5,503
Intercept b:	0,091
Correlation coefficient r:	0,9999
Result uncertainty:	33,3%
Probability of error (a):	5,00%
Number of injections:	2

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Limit of detection: 0,2mg/L

These results show that the TOC-CPH with high sensitivity catalyst covers the required linear dynamic range from 0,2 – 20mg/L. This means both applications, purified water and this extraction solution can be measured with a single TOC-L CPH instrument.

■ Recommended Analyzer / Configuration

TOC-L $_{CPH}$ with high sensitive catalyst
ASI-L (40ml), external sparge kit

■ **Source**: www.usp.org

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3. Chemical industry

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 develop 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 problems. 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.’

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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.

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.

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 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.

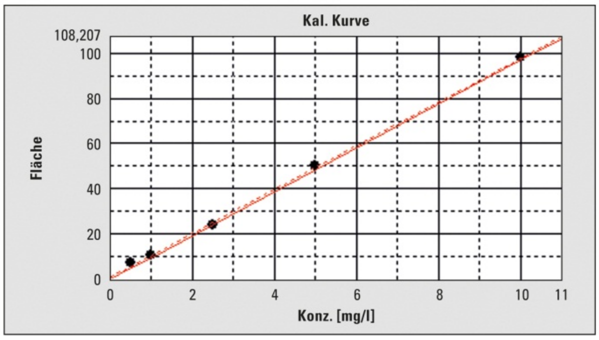

Abb.2 Mehrpunktkalibration mit Verdünnungsfunktion

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).

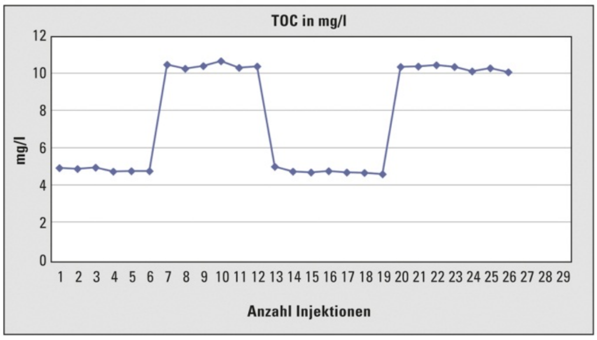

Fig.3: Results of original and spiked hydrochloric solution

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.

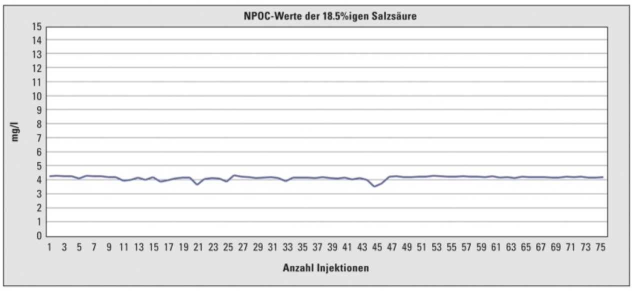

Fig.4: Result of longterm stability

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

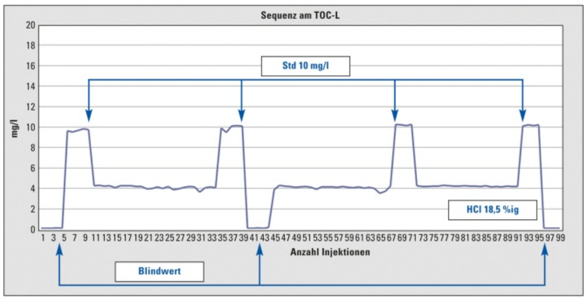

Fig. 5: Sequence of hydrochloric acid, blank (pure water) and Standards (10 mg/l)

■ Recommended analyzer / configuration

- TOC-L_{CPH} with a normal sensitive catalyst (without glass wool at the bottom of the catalyst tube)
- B-Type scrubber with $SnCl_2$ solution
- Copper bead scrubber with pH paper
- Bypassing the blank check vessel
- Substituting water for phosphoric acid (IC vessel)
- OCT-L 8-port sampler

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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_3 solution with a detection limit of < 10 mg/L.

■ Sample preparation

For sample preparation, the 69% HNO_3 solution was diluted to a ratio of 1:10 with ultrapure water.

Compound (concen-tration)	Dilution	Conz. [%]
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.

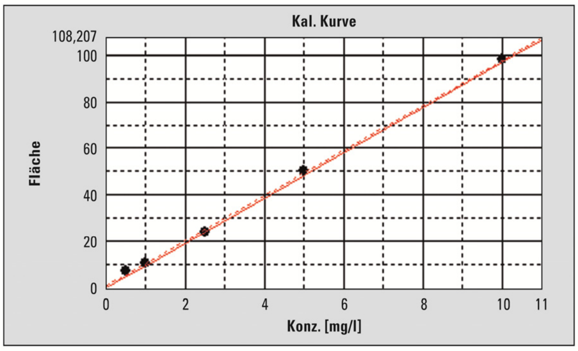

Fig. Multi-point calibration with dilution function

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

■ Matrix interferences

In addition to CO_2, various nitrogen oxides are formed from the organic components during the combustion of nitric acid. Excessively high levels of NO_3 can lead to significant amounts of N_2O (nitrous oxide). Nitrous oxide exhibits absorption bands in the same IR detection range as CO_2 and can, therefore, be misinterpreted for CO_2. In addition, nitrous oxide can cause tailing and can affect the peak symmetry.

Due to the high solubility of N_2O 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 $_{CPH}$ 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_2 vapors. SO_2 exhibits absorption bands in the same IR detection range as CO_2 and can, therefore, be misinterpreted for CO_2.

To determine organic contaminations in highly concentrated sulfuric acid, additional SO_2 scrubbers are used.

The following SO_2 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_2.
- Mist scrubber (cartridge)
  Just like the halogen scrubber, the 'Mist scrubber' is used in the flow line for SO_2 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 (Concen-tration)	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.

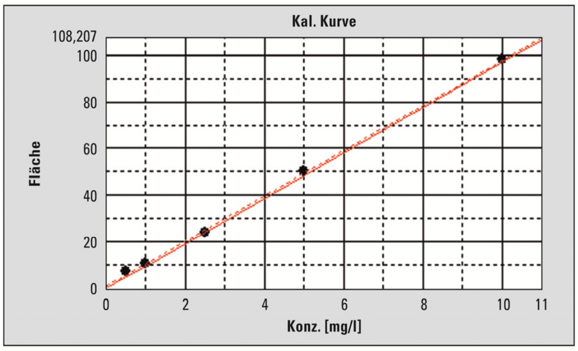

Fig. Multi-point calibration with dilution function

■ Kit for high-salt samples

For the determination, a $TOC\text{-}L_{CPH}$ 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 $NaSO_4$ 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 $_{CPH}$
OCT-L
High-Salt-Kit
B-Type-Scrubber with diluted hydrochloric acid with wire net.
Mist-Scrubber

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Application News

No. SCA-130-304

Sum parameter – Total Organic Carbon

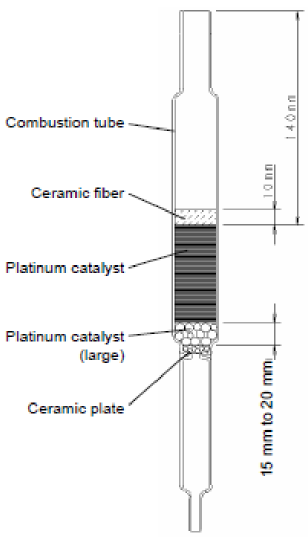
TOC – Determination in brines

The determination in difficult matrices, such as brines or heavily contaminated waste-waters, 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 ia 801 °C, $NaSO_4$ 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_2SO_4	888°C
$MgCl_2$	708°C
$CaCl_2$	782°C
K_2SO_4	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 (Concen-tration)	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$_{CPH}$ 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.

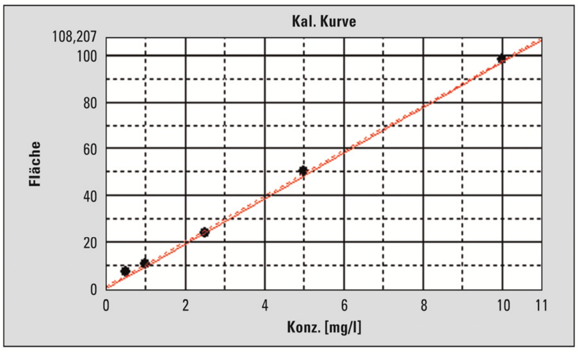


Fig. Multi-point calibration with dilution function

■ 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

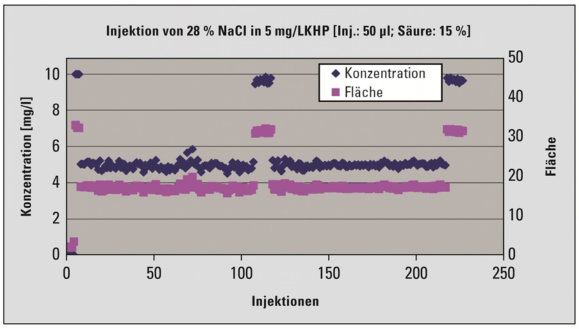
■ Stability test

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$_{CPH}$
High-Salt-Kit
B-Type-Scrubber

Application News

Sum parameter – Total Organic Carbon

TOC – Determination in sodium hydroxide solution

No. SCA-130-305

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_2 from the environment. As air contains approximately 400 ppm CO_2, 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 (Concen-tration)	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.

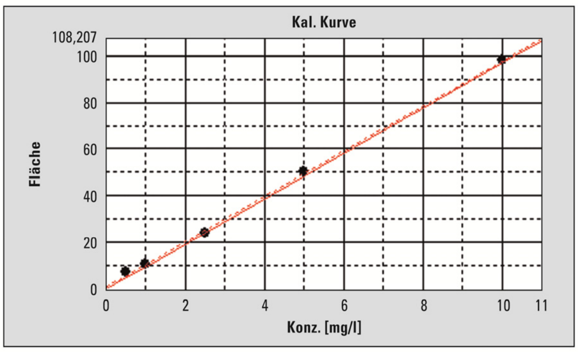
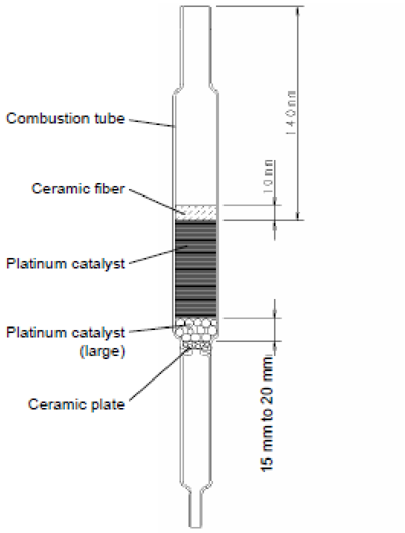


Fig. Multi-point calibration with dilution function

■ Kit for high salt samples

For the determination, a TOC-L_{CPH} 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 $NaSO_4$ 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.

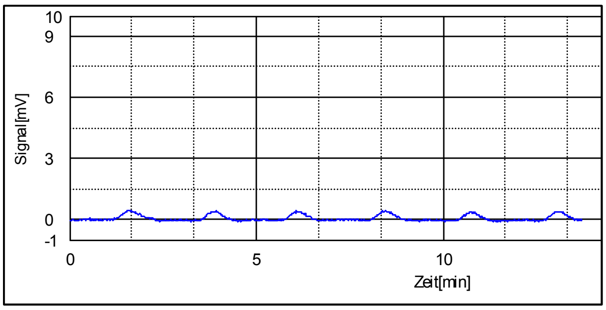


Fig. Example peaks of 50% sodium hydroxide solution

■ Recommended Analyzer / Configuration

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

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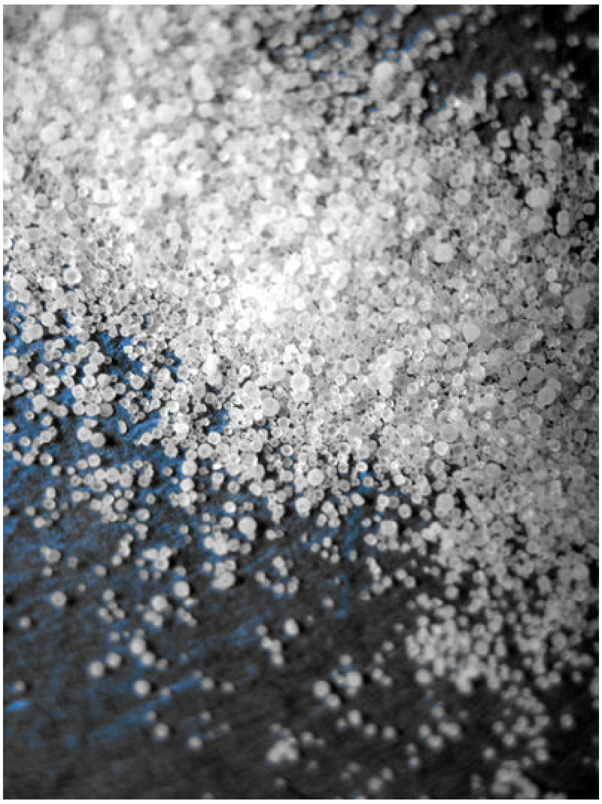
Application News

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 (Concen-tration)	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.

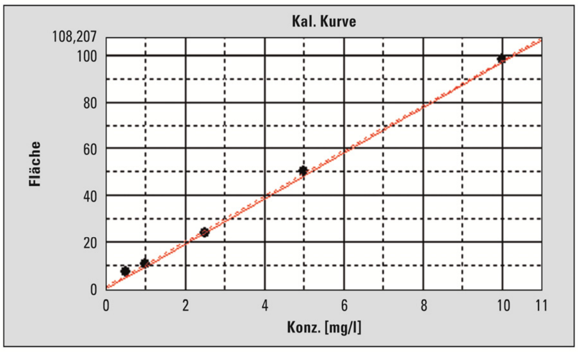
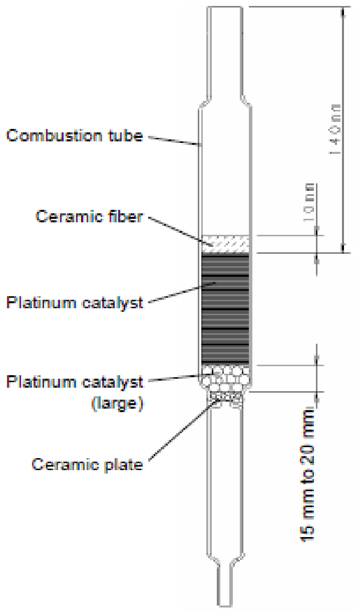


Fig. Multi-point calibration with dilution function

For the determination, a TOC-L$_{CPH}$ 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 $NaSO_4$ (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

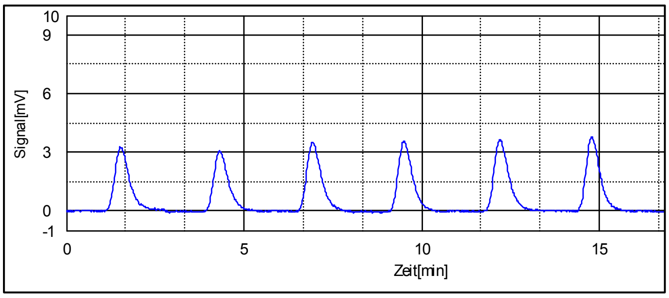


Fig. Peak graphs of a diluted soda solution (ca.5%)

■ Recommended Analyzer / Configuration

TOC-L $_{CPH}$
ASI-L
High-Salt-Kit
B-Type- Scrubber

Application News

No. SCA-130-307

Sum parameter – Total Organic Carbon

TOC – Determination in ammonia or ammonium salt solutions

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 (Concen-tration)	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.

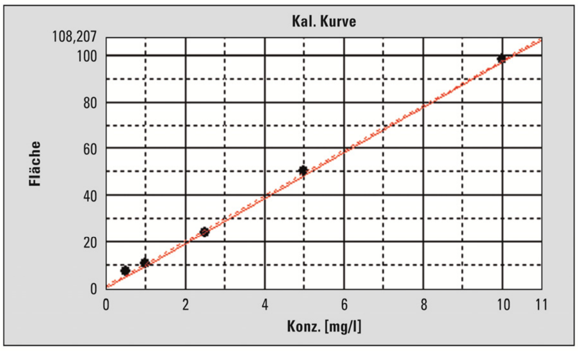


Fig. Multi-point calibration with dilution function

■ Interferences

In addition to CO_2 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_2O (nitrous oxide). Nitrous oxide exhibits absorption bands in the same IR detection range as CO_2 and can, therefore, be misinterpreted for 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 N_2O 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

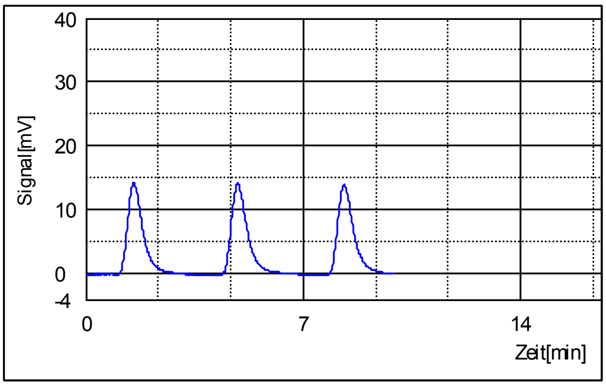


Fig. Example peaks of 40% ammonium nitrate solution

■ Recommended analyzer / Configuration

TOC-L $_{CPH}$

OCT-L (8-port sampler)

B-Type- Scrubber

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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 (Concen-tration)	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.

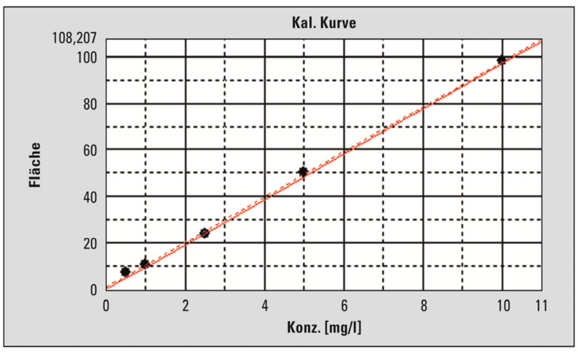
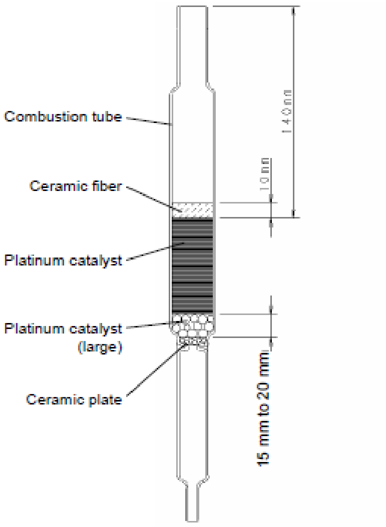


Fig. Multi-point calibration with dilution function

■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 $NaSO_4$ (888 °C) compared to 801 °C of 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 CO_2 and can, therefore, be misinterpreted for 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 N_2O 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

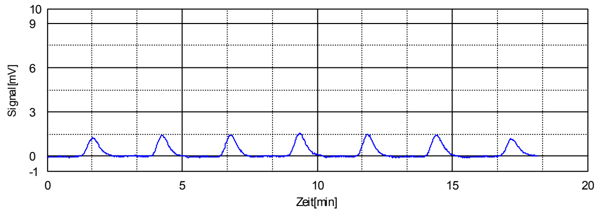


Fig. Example peaks: Sodium nitrate

■ Recommended Analyzer / Configuration

TOC-L_{CPH}
ASI-L
High-Salt-Kit
B-Type-Scrubber

Application News

No. SCA-130-309

Sum parameter – Total Organic Carbon

TOC determination in phosphoric acid

Phosphoric acid is one of the most frequently used inorganic acids in industrial applications. It is applied as starting material for the manufacture of phosphate-containing fertilizers as well as for the production of water-softening agents such as detergent additives.
Phosphoric acid is also used in the food industry – as acidification agent and preservative in beverages or as antioxidant in meats and meat products.

Particularly for these types of applications, it is important to apply acids that are pure and free from foreign substances. Manufacturers and processors of phosphoric acids are increasingly using the TOC (Total Organic Carbon) sum parameter for quality control. This parameter is a measure of the contamination of phosphoric acids by organic components.
The TOC method by using the catalytic combustion is not suitable for the determination of phosphoric acid, because the phosphoric acid damages the combustion tube and the catalyst.
Due to this, the wet chemical TOC method is used to measure TOC in phosphoric acid.

■ Wet-chemical UV oxidation at 80 °C

The determination of the TOC content in phosphoric acid is carried out via wet-chemical UV oxidation using Shimadzu's TOC-V_{WP}.

Its core technology is the powerful oxidation applying a combination of sodium persulfate and UV oxidation at 80 °C. This ensures that all dissolved carbon compounds are converted to CO_2.

In the presence of persulfate ions and UV illumination, OH-radicals are formed which have a strong oxidative effect and convert organic compounds to carbon dioxide. A carrier gas transports the carbon dioxide formed to the NDIR detector where they are detected.

Automated reagent preparation eliminates any contamination of the reagent solutions and minimizes the blank value of the instrument.

■ TOC determination

Due to lower TOC concentration, the instrument is calibrated in a range of 0,1 – 1 mg/L.

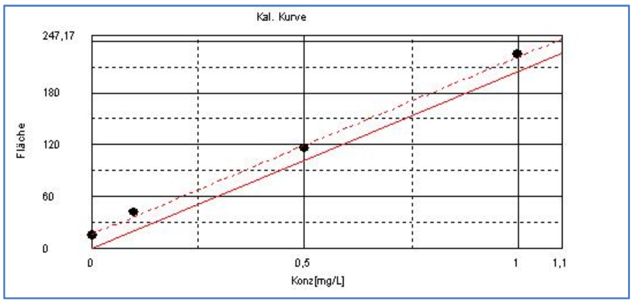


Figure: Calibration of NPOC between 0,1 – 1 mg/l.

Concentration of the phosphoric acid does not play a significant role in the determination; it is only necessary to ensure that the acid is not too viscous. The 85% phosphoric acid solution was therefore diluted 1:5 with water.

The resulting 17% acid solution was transferred into the instrument using an OCT-1 autosampler.

The autosampler OCT-1 has a big advantage for the measurement of aggressive matrices, because its parts are done of Teflon.

■ Method of phosphoric acid measurement

The concentrated phosphoric acid (85%) is diluted by 1:5.

TOC determination in phosphoric acid was carried out using the NPOC (Non-Purgeable Organic Carbon) method. Prior to TOC determination, neutral or alkaline samples are acidified in order to decompose all inorganic carbonates and bicarbonates. This step could be omitted for phosphoric acid.

Acidification:	0%
Sparge-time:	2 minutes
Injection volume:	3000µl

■ Results

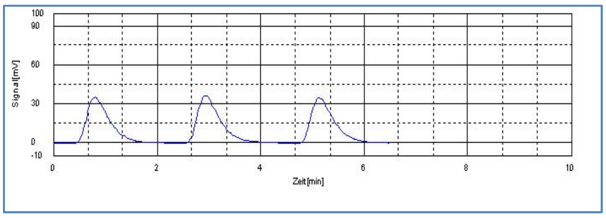


Abb.: Peak graph of diluted phosphoric acid(17%)

The 17% phosphoric acid solution measured in this way resulted in a TOC concentration of 0.61 mg/L. The relative standard deviation over three injections was 1.8%.

■ Recommended Analyser / Configuration

- TOC-$V_{WP/WS}$
- OCT-1

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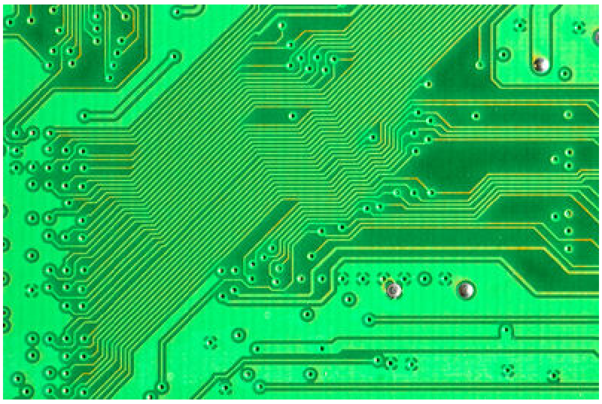
Application News

No. SCA-130-310

Sum parameter – Total Organic Carbon

TOC – Determination in diluted hydrofluoric acid

Hydrofluoric acid is the only acid that attacks glass (glass etching). Because of this chemical property, it plays a distinct role in several industrial processes, for instance in the manufacturing of solar cells and wafers as well as in microchip production. Hydrofluoric acid is the most widely used etching agent in the semiconductor industry.



When carrying out etching processes, it is important to ensure that the etching agent used will etch the respective layers and not leave any contaminants.

This raises questions on the impurities of etching agents, where both the purity of the starting acid and that of the etching solutions after the etching process are of interest.

To determine the degree of contamination, the TOC parameter is particularly suitable, as it is a sum parameter that detects all organic carbon compounds.

■ TOC determination

In the following measurement, a 4% hydrofluoric acid was manually diluted to 1:10 with water and measured using the TOC-L_{CPH}. Given the acidity of the hydrofluoric acid, the IC content can be neglected. With regard to the dilution, the solution was slightly acidified and sparged for 3 minutes. The NPOC was subsequently determined by means of combustion oxidation.

An aliquot of the sample is injected onto a hot (680 °C) platinum catalyst. The organic substances are converted to CO_2 and detected via an NDIR detector.

■ Calibration

Due to mostly working in a small measuring range, calibration was carried out in a range of 0.25 mg/L – 5.0 mg/L. For dilutions, the automatic dilution function of the TOC-L system was applied. The injection volume was 150 µL respectively.

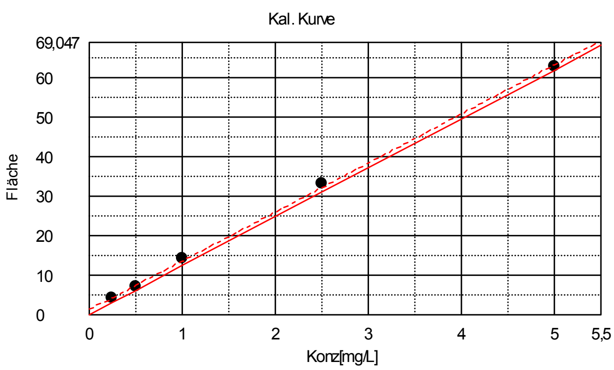


Figure: Calibration curve, TC 5 mg/L.

■ Measurement example

A total of 3 different hydrofluoric acids (0,4%) were measured:

- Hydrofluoric acid prior to etching (**HF1**)
- Hydrofluoric acid after etching (a seemingly clean wafer (**HF2**))
- Hydrofluoric acid after etching (a seemingly dirty wafer (**HF3**))

■ NPOC method

Acidification: 1.5%
Purging time: 3 minutes
Injection volume: 150 µL
Number of injections: 3

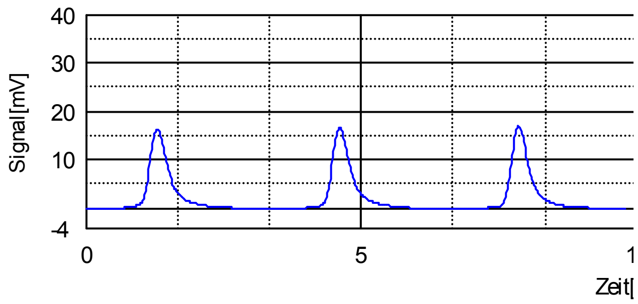


Figure: Peaks of the diluted HF solution.

The measurements were already stable after two or three injections. It is advantageous to carry out several HF injections prior to the actual sample measurement.

■ Results

Sample	NPOC [mg/L]	RSD [%]
HF 1	2.42	4.8
HF 2	3.09	3.2
HF 3	4.38	2.1

■ Protection and safety

For such measurements, comprehensive protective measures for dealing with hydrofluoric acid must be urgently observed. This also includes wearing protective clothing, gloves and safety goggles.

After measurement, the instrument must be rinsed several times with water. In addition, 20 injections with ultrapure water must be carried out.
Nevertheless the lifetime of syringe, combustion tube and catalyst will be shortening, due to HF solution.

■ Recommended instrument/ equipment

TOC-L$_{CPH / CPN}$
OCT-L

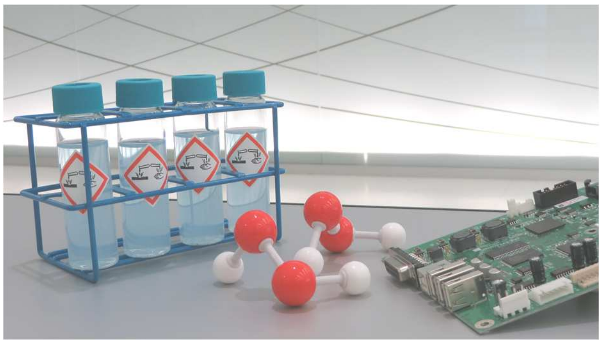
Application News

No. SCA-130-311

Sum parameters – Total Organic Carbon

Combined TOC and TN_b determination in hydrogen peroxide solution (H_2O_2)

Hydrogen peroxide (H_2O_2) is a mostly odorless, colorless liquid which could be described simply as water with an additional oxygen atom attached. This additional oxygen atom is keeping the molecule barely together in the so-called peroxide bond, but defines its large variety of uses in chemistry as a potent oxidizing agent. As the only byproducts of its reactions are water and oxygen, it can be considered environmentally friendly when used properly.



■ Economic importance of H_2O_2

Hydrogen peroxide is frequently used as a bleaching agent of pulp, natural fiber and chemical fibers in both industrial and household applications. In water treatment, in so called UVOX-processes (UV and Oxidation), UV radiation causes the formation of hydroxyl radicals that are used to decompose organic impurities in drinking water. Additionally, it is used in the synthesis of chemical materials, pharmaceuticals, as rocket propellant, disinfectant, in metal surface treatment and many more.
Hydrogen peroxide tends to decompose into water and oxygen with increasing pH value, but especially when coming into contact with metal surfaces, causing a catalytic reaction. That is why stabilizers (organophosphorus compounds and others) are being added to commercially available H_2O_2 solutions, creating a wide range of available purity levels for various applications.

The level of purity required in the various industrial fields is becoming increasingly higher, a strong example being the semiconductor industry. To determine the purity of hydrogen peroxide solutions, combined TOC and TN_b measurement is an effective tool, as meaningful results can be obtained within minutes.

■ TOC / TN_b determination

In the following measurements, a 30% hydrogen peroxide solution was measured using a Shimadzu TOC-L CPH with TNM-L module.
Calibration of the system was carried out using the automatic dilution function within a range of 10 – 50 mg/L TOC and 1 – 10mg/L TN_b.

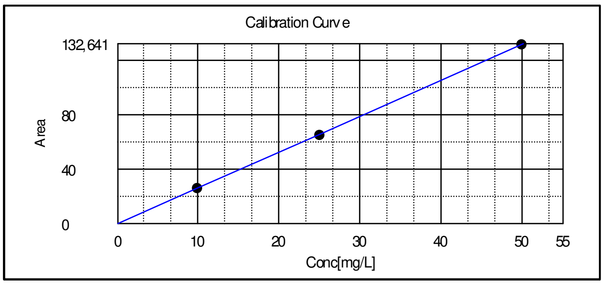


Fig.1: TOC Multi-point calibration with dilution function

The undiluted hydrogen peroxide solution is placed in the autosampler in septum-sealed 40mL vials. The sample is then acidified and sparged out to remove inorganic carbon and CO_2 using the external sparge kit (NPOC determination). An undiluted aliquot of the sample is injected onto a hot (720°C) platinum catalyst. Organic substances are converted to CO_2 and detected using a NDIR detector. At the same time, nitrogen compounds are converted to NO and detected by a chemiluminescence detector.

■ Measurement method and results

Measurement type: NPOC
Addition of acid: 1.5%
Sparge time: 5 minutes
Injection volume.: 50 µL

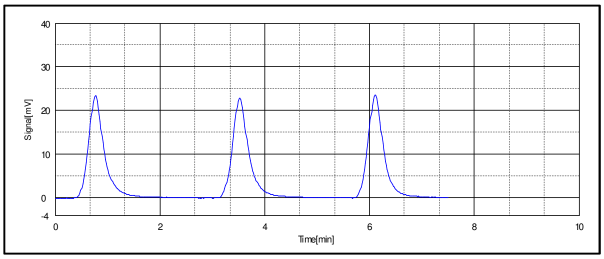


Fig.2: 3 NPOC Injections of 30% H_2O_2.

Multiple injections of the untreated 30% hydrogen peroxide solution were conducted successfully and with good reproducibility.

To investigate matrix influences, a potassium hydrogen phthalate solution was subsequently added to increase the TOC content by 10 and 20mg/L respectively. Concurrently, a mixed Potassium nitrate and Ammonium sulfate solution was added to increase the TN_b by 1 and 2mg/L (Figure 3).

Sample	NPOC [mg/l]	TN_b [mg/l]	RSD [%]
H_2O_2 (30%)	19,4	2,76	1,0
H_2O_2 (30%) (spiked with 10mgC/l and 1mgN/l)	29,0	3,71	1,5
H_2O_2 (30%) (spiked with 20mgC/l and 2mgN/l)	38,9	4,71	0,5

Fig.3: Results of original and spiked H_2O_2

The NPOC and TN_b contents were found precisely according to the added amounts. The validity and efficiency of the measurement method was thereby considered verified.

■ Further considerations

The oxidation products of H_2O_2 pose no harm to the liquid handling system, catalyst and detectors of the TOC-L. The samples themselves however should be placed in septum-sealed vials in the autosampler, to exclude accidental spilling of the aggressive substance.
The injection volume for both TOC and TN_b determination can be increased further to be able to measure in lower ranges.

Higher concentrated solutions (e.g. 55%) can be measured as well. Unstabilized solutions might tend to create foam when applying the NPOC method. In such cases it is advised to use the difference method (TOC=TC-IC) to prevent bad reproducibility.

■ Recommended analyzer / configuration

TOC-L_{CXH}
TNM-L for TN_b determination
ASI-L with external sparge kit

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4. TOC special applications

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.'

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Application News

No. SCA-130-401

Sum parameter – Total Organic Carbon

TOC-determination in algal biomass – suspension method

The excessive global CO_2 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_2 into biomass using photobioreactors.

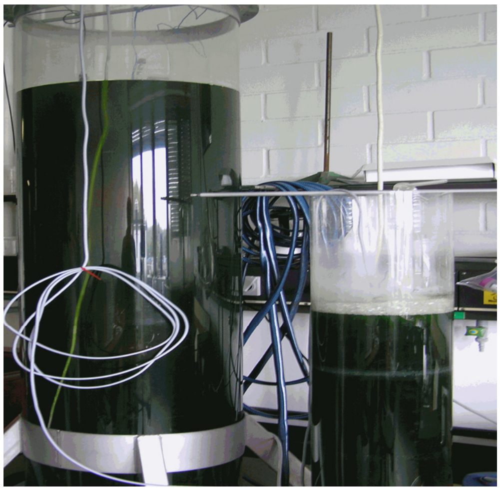
The CO_2 gas is introduced into the photobioreactor in order to be used for the growth of algae. The biomass, or algae, can be used in many different application areas: in the cosmetics industry, the construction industry, and the food segment, in agriculture as fertilizer or for energy utilization.

■ Test methods for implementation

The efficiency of the photobiorectors 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

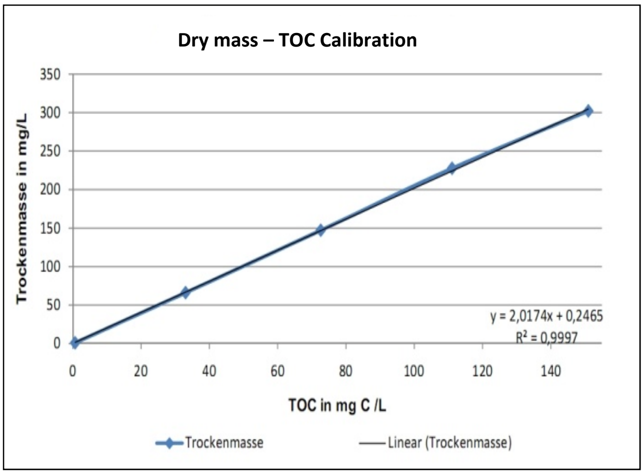
■ Sample preparation

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.

■ Corrrelation

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

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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 (Nl/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

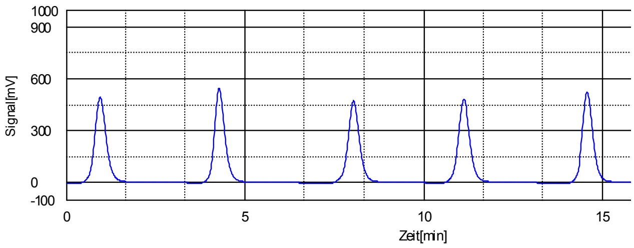

Fig. NPOC-Peaks of suspension

■ TN_b-Determination

The TOC determination using catalytic combustion oxidation allows the simultaneous measurement of the total bound nitrogen (TN_b), since, in addition to the carbon dioxide from organic substances, NO is formed from nitrogen-containing compounds. For the conversion of NO to NO_2, 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_b value. Nitrogen compounds also play an important role when it comes to liquid manure.

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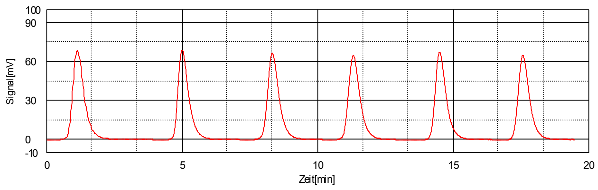

Fig.4: Peak graphs of TN-determination

Simultaneously with the organic content, the TN_b was determined (duplicate determination from two different approaches with 5 separate injections each) yielding the following results:

Liquid manure (dried and powdered)	TN_b [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 $_{CPN}$ with normal sensitive Catalyst
for TN_b-Determination: TNM-L Module
ASI-L (40ml) with stirrer option and external Sparge-Kit.

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Application News

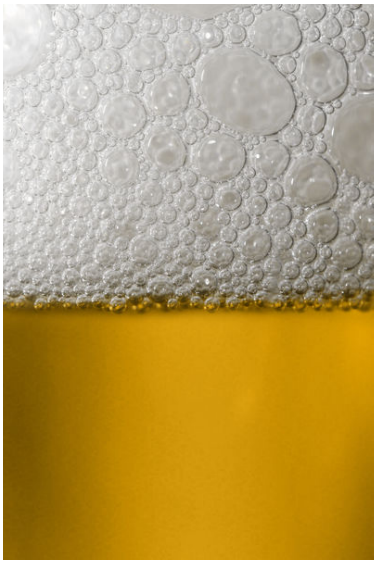
No. SCA-130-403

Sum parameter – Total Organic Carbon

Carbon dioxide determination in beer

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_2 content of a beer affects the threshold values for various fragrance and aroma components. In addition, bottling under CO_2 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_2 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_2 (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_2.

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

Preservation step:

$$CO_2 + OH^- \rightarrow HCO_3^-$$

$$CO_2 + 2\,OH^- \rightarrow CO_3^{2-} + H_2O$$

In the TOC analyzer, the sample is injected in a concentrated phosphoric acid solution (25%). The CO_2 is subsequently released again and is transferred via the carrier gas to a CO_2-selective NIDR detector where it is detected.

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

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

$$CO_3^{2-} + 2\,H^+ \rightarrow H_2O + CO_2$$

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

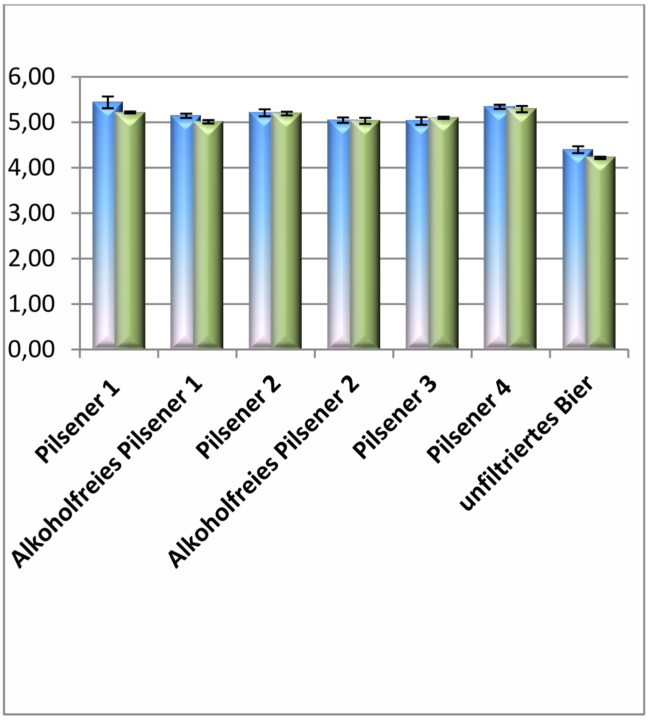
- can be automated to a high degree
- fast
- good reproducibility and high accuracy (precision)
- multiple determinations from one sample is possible
- effortless calibration
- simple operation
- highly specific

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 CPH
ASI-L (40ml)

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Shimadzu Europa GmbH
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Application News

Sum parameters – Total Organic Carbon

TOC-determination in water for the production of beverages

No. SCA-130-404

Water is the most popular non-alcoholic beverage in the world. However, there are considerable differences in the different types of water, their origin and especially their quality.

Bottled water may be called *natural mineral water* in the EU, if it originates from underground deposits which are protected from contamination and if it is bottled directly at the well. It may be enriched with CO_2, but possible water treatment steps are severely limited according to the applicable regulations, while the purity of the water, its content of minerals and trace elements as well as other ingredients are subject to labelling. Natural mineral water may only be marketed if it is officially certified.

Table water is a type of water that does not meet the requirements of natural mineral water. Using food additives, it may be enriched with minerals, trace substances and CO_2. Natural mineral water as well as drinking water from the public supply network can be used to produce bottled water, the latter being the more common method depending on the location of the production site.

Soft drinks such as fruit juice, soda and other water-based mixed drinks, are also popular thirst quenchers that are subject to strict quality standards. Here again, natural water or drinking water are used as feedstock for the production. The quality of these waters can have significant impact on the quality of the final product.

The parameter TOC can serve as an indicator for the content of organic matter present in water from natural sources, such as well or mineral water. In the following example, 4 different types of water used in the production of beverages were analysed using a Shimadzu TOC-L Series total organic carbon analyser.

▪ Analytical method

The samples were analysed using the NPOC method, thus removing the inorganic carbon content TIC (carbonates, hydrogen carbonates and dissolved CO_2) before the actual analysis. Acidification and sparging of the sample is handled fully automatically by the ISP module (integrated sample preparation) of the TOC-L. In addition to the automatic sample preparation, this system allows the automatic dilution of samples and calibration standards as well. This reduces the workload for the laboratory personnel.

Calibration

The instrument was calibrated using a potassium hydrogen phthalate stock solution, using the automatic dilution function, at carbon concentrations of 0, 0,3, 1,0, 2,0 and 3,0 mg/L (Fig1.). In order to eliminate the influence of carbon impurities in the ultra pure water used to prepare the standard solutions, the calibration curve was shifted in parallel through the coordinate origin.

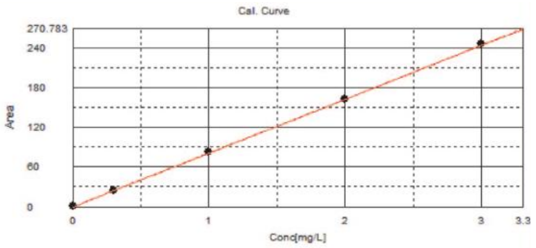

Fig.1: 5-point calibration in range 0 to 3mg/L

Method parameters

Method: NPOC
Acidification: 1,5%
Injection volume: 1.000µl
Sparge time: 1,5min (in the syringe)
No. of Injections: 3 / Max. 5

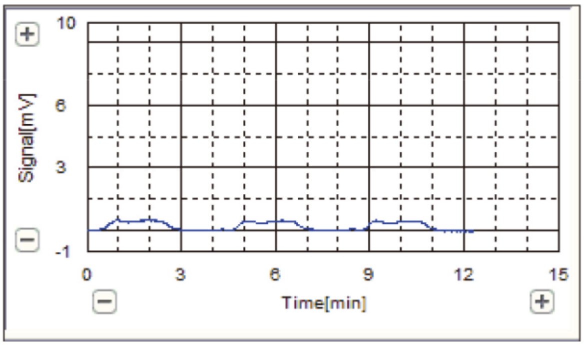

Fig.2: 3 NPOC-Injections of spring water

Results

The analysis of the different water types using the NPOC method yielded meaningful results within a few minutes. All TOC concentrations were within a low range between 0,004 and 0,3mg/L, but could be determined with very low standard deviations (Fig.3).

Sample	NPOC [mg/l]	SD [mg/l]
Table water	0,108	0,003
Deep well water	0,042	0,006
Spring water	0,063	0,002
Natural mineral water	0,281	0,001

Fig.3: NPOC-Concentrations of the various water types

TOC analysis allows the manufacturers of beverages to easily and quickly assess the content of organic contaminants in their feedstock, thus helping to optimize production processes and further ensure product quality.

Recommended instrument / configuration

TOC-L $_{CPH}$
ASI-L

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LAAN-A-TC-E026

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Application News

No.O49

Total Organic Carbon Analysis

Monitoring of Algae Growth by TOC Measurement

Global warming due to the excessive use of fossil fuels is becoming a problem which has prompted and accelerated the search for alternative fuels. Among the more attractive alternatives is biomass fuel, which is attracting considerable attention. Microalgae can be used for the production of oil without competing with food production, and to a greater extent than other biofuels, its productivity per unit time and area is high, while arable land selection possibilities are great. As for the practical use of microalgal biomass, various studies have been conducted at each stage of its production, including stock selection and breeding, cultivation, harvesting, oil extraction, and purification.
The Shimadzu TOC-L Series combustion-type total organic carbon analyzer, with its powerful organic substance oxidation features, permits the complete oxidization and measurement of samples such as microalgae cell culture suspensions.
Here, we introduce an example of a unique application in which the TOC-L_{CPH} total organic carbon analyzer is used to track the growth process of microalgae by directly measuring, without conducting any pretreatment, the TOC content in a suspended culture of microalgae cells.
The data presented here was provided by the University of Tsukuba Shiraiwa laboratory.

T. Iharada, M. Tanaka

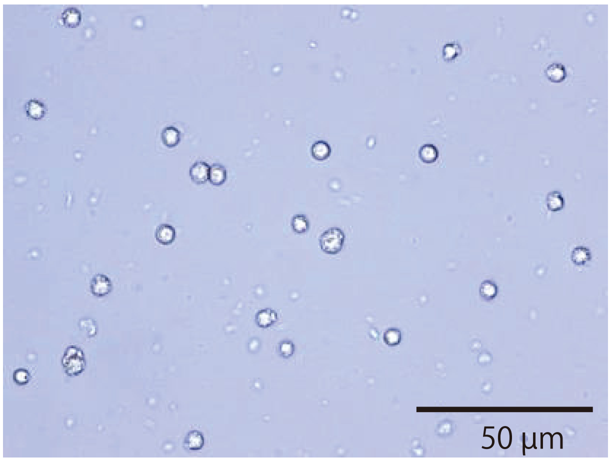

Fig. 1 Algae

Analytical Method

The microalgae was cultured for 8 days, and from the starting day, TOC measurement was conducted once per day for both Sample 1, which consisted of culture along with suspended microalgae cells, and Sample 2, which consisted of culture only obtained by removing the microalga cells from Sample 1 through centrifugal sedimentation. Then, from the difference in organic carbon (TOC) between Sample 1 and Sample 2, we obtained the value of TOC present in the organic matter of the microalgae cells. Further, we measured the turbidity of Sample 1, and that value was taken as an index of cell mass.
A microscopic image of the microalgae cells of Sample 1 is shown in Fig. 1.

Measurement Results

Fig. 2 shows the measurement results for the total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) associated with the cell mass during the culture period. Also, the ratios of TOC to IC in the microalgae cells are shown in Fig. 3. From these results, it was possible to obtain information regarding the increase and decrease of TC, IC and TOC values associated with the microalgae cells throughout the culture process.
One essential element in the practical realization of microalgal biomass is establishment of the culture conditions, and it is clear from this study that information regarding the carbon balance can be obtained using a TOC analyzer.

<Measurement Conditions>

Analyzer	: Shimadzu TOC-L_{CPH} total organic carbon analyzer
Catalyst	: Standard catalyst
Measurement item	: TOC (TC–IC)
Calibration curve	: 1-point calibration curve using 1000 mg/L potassium hydrogen phthalate aqueous solution
Sample 1	: Culture solution containing suspended microalgae cells
Sample 2	: Culture solution with microalgae cells removed using centrifugal sedimentation
Water sampling method	: Sample 1 water was sampled while stirring with a magnetic stirrer

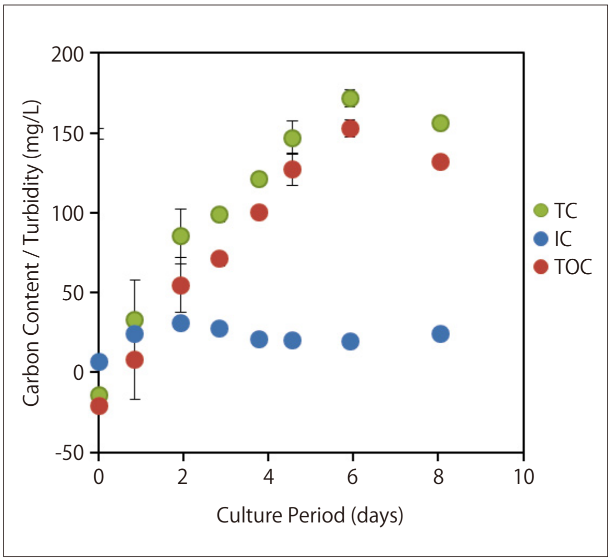

Fig. 2 Changes in TC, IC, TOC Quantity in Microalgae Cells (Conversion value per turbidity unit)

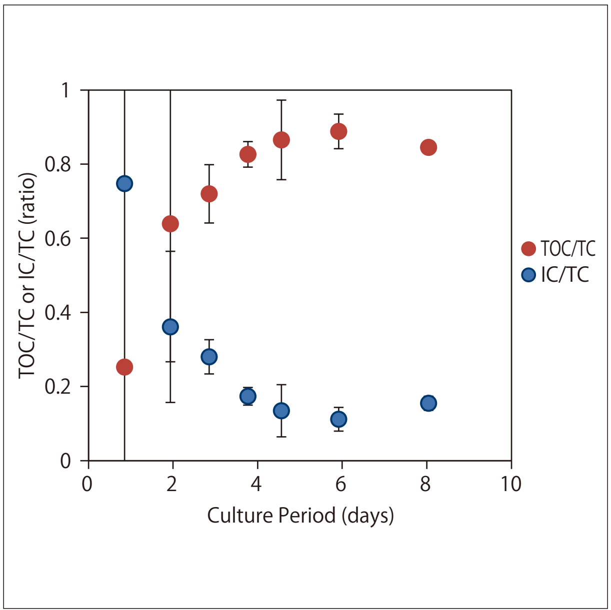

Fig. 3 Changes in TOC/TC and IC/TC in Microalgae Cells

Shimadzu TOC-L Series Total Organic Carbon Analyzer

The Shimadzu TOC-L Series Total Organic Carbon Analyzer can be used to conduct the following types of measurements.

- Measurement of total carbon and nitrogen content in water, quantity dissolved, quantity suspended*
- Measurement of total carbon, organic carbon, inorganic carbon in water
- Measurement of dissolved CO_2 in water

Thus, the TOC-L series can be utilized for such applications as the following types of microalgae research.

- Obtain information related to the physiological state and the properties of microalgae.
- Understand the changes in cell material with respect to changes over time in the culture and changes due to light and dark environment.
- Understand quantitatively the carbon and nitrogen balance in the culture system.

The TOC-L Series instruments can be used to conduct measurements using very small volumes of sample in the range of 10 to 20 mL, making it suitable for laboratory-scale studies.

* The TNM-L Total Nitrogen Unit option is required for nitrogen (TN) measurement. In addition, filtering and centrifugal separation, etc. are required for separate measurement of samples in the dissolved state and suspended state.

Fig. 4 TOC-L Total Organic Carbon Analyzer + TNM-L Total Nitrogen Unit

First Edition: Apl. 2014

LAAN-A-TC-E027

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Application News

No.O50

Total Organic Carbon Analysis

Characterization of Algae by TOC Measurement

Global warming due to the excessive use of fossil fuels is becoming a problem which has prompted and accelerated the search for alternative fuels. Among the more attractive alternatives is biomass fuel, which is attracting considerable attention. Microalgae can be used for the production of oil without competing with food production, and to a greater extent than other biofuels, its productivity per unit time and area is high, while arable land selection possibilities are great. As for the practical use of microalgal biomass, various studies have been conducted at each stage of its production, including stock selection and breeding, cultivation, harvesting, oil extraction, and purification.
The Shimadzu TOC-L Series combustion-type total organic carbon analyzer, with its powerful organic substance oxidation features, permits the complete oxidization and measurement of samples such as microalgae cell culture suspensions.
Here, we introduce an example of a unique application in which the TOC-L_{CPH} total organic carbon analyzer is used to characterize microalgae by directly measuring, without conducting any pretreatment, the TOC content in a suspended culture of microalgae cells.
The data presented here was provided by the University of Tsukuba Shiraiwa laboratory.

T. Iharada, M. Tanaka

Analytical Method

Five types of microalgae A – E were cultured for 3 to 14 days, and at the start, after several days, and at the end of culturing, TOC measurement was conducted for sample 1, consisting of the various types of microalgae cells suspended in culture medium, and for sample 2, consisting of culture obtained by removing the microalga cells through filtration of sample 1. Then, from the difference in organic carbon content (TOC) in samples 1 and 2, we determined the TOC in the organic material of the various types of microalgae cells. Also, the turbidity of sample 1 was measured, and that value was taken as an index of cell mass.

<Measurement Conditions>

Analyzer	: Shimadzu TOC-L_{CPH} total organic carbon analyzer
Catalyst	: Standard catalyst
Measurement item	: TOC (TC–IC)
Calibration curve	: 1-point calibration curve using 1000 mg/L potassium hydrogen phthalate aqueous solution
Sample 1	: Culture solution containing suspended microalgae cells
Sample 2	: Culture solution with microalgae cells removed by filtration
Water sampling method	: Sample 1 water was sampled while stirring with a magnetic stirrer.

Measurement Results

The increase in total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) in five types of microalgae culture and cells are shown in Fig. 1 and Fig. 2, respectively.
It became apparent from the results that organic material take-up and release by the cells varied depending on the type of microalgae and the duration of the culture period. Further, in regard to the microalgae that form the shells of calcium carbonate, the results suggested that such shell formation information can be obtained using IC measurement.
To express these pieces of information that include the type, nature and growth state of microalgae, a TOC analyzer can be utilized for screening of the microalgae and investigation of culture conditions.

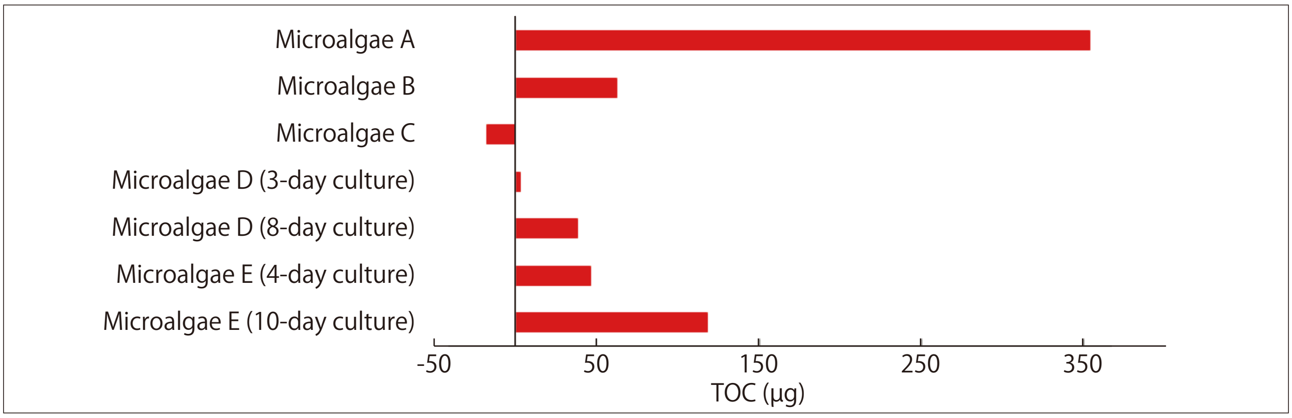

Fig. 1 TOC/OD in Culture (Conversion value per turbidity unit)

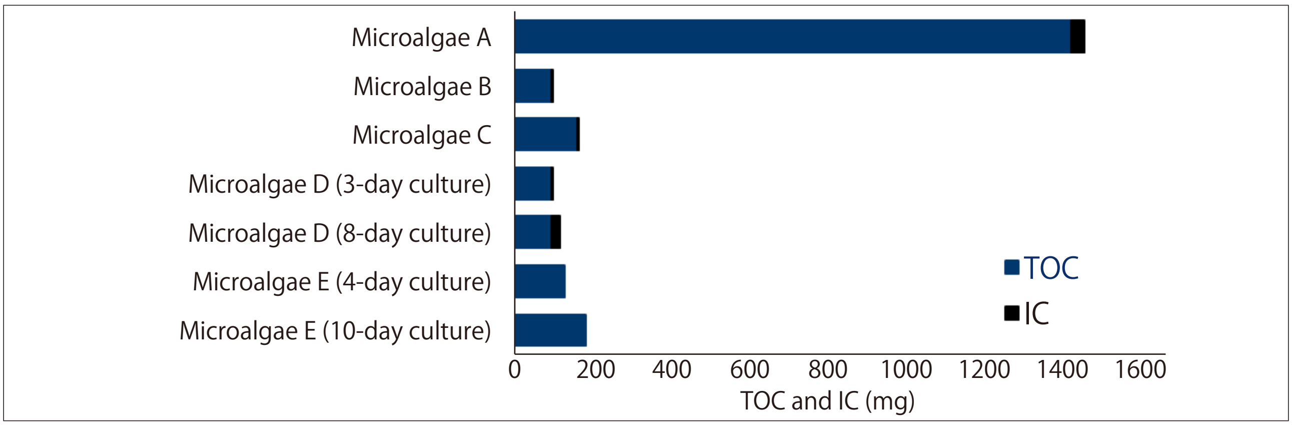

Fig. 2 TOC and IC/OD in Cell (Conversion value per turbidity unit)

Shimadzu TOC-L Series Total Organic Carbon Analyzer

The Shimadzu TOC-L Series Total Organic Carbon Analyzer can be used to conduct the following types of measurements.

- Measurement of total carbon and nitrogen content in water, quantity dissolved, quantity suspended*
- Measurement of total carbon, organic carbon, inorganic carbon in water
- Measurement of dissolved CO_2 in water

Thus, the TOC-L series can be utilized for such applications as the following types of microalgae research.

- Obtain information related to the physiological state and the properties of microalgae.
- Understand the changes in cell material with respect to changes over time in the culture and changes due to light and dark environment.
- Understand quantitatively the carbon and nitrogen balance in the culture system.

The TOC-L Series instruments can be used to conduct measurement using very small volumes of sample in the range of 10 to 20 mL, making it suitable for laboratory scale studies.

* The TNM-L Total Nitrogen Unit option is required for nitrogen (TN) measurement. In addition, filtering and centrifugal separation, etc. are required for separate measurement of samples in the dissolved state and suspended state.

Fig. 3 TOC-L Total Organic Carbon Analyzer + TNM-L Total Nitrogen Unit

First Edition: Apl. 2014

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Shimadzu Corporation
www.shimadzu.com/an/

Application News

No. SCA-130-407

Sum parameters – Total Organic Carbon

Cleaning validation in the food and consumables industries

Many everyday necessities, such as different types of food, personal care products or cosmetics, are produced in a discontinuous process. As soon as one batch is completed and sent to further processing or filling, the production equipment and machines are being cleaned. The successful cleaning of the production equipment is mandatory, before the production of the next batch can be started.

Numerous trade chains offer so-called private labels which are produced in contract manufacturing. It happens that a private label manufacturer works for several trade chains and manufactures different products or manages different mixtures and formulas using the same production systems. In this case, it must be ensured that the production systems are cleaned prior to manufacturing the next product.

The 'International Featured Standards' (IFS) define quality standards to ensure that the products requested by the customer company comply with all the required specifications. Several documents set the standards for quality assurance, such as 'IFS Food' or the 'IFS HPC' (Household and Personal Care) standard for the production of household or personal care products.

■ IFS Food

Cleaning of production plants is also addressed by the IFS Food standard. Chapter 4.10 'Cleaning and disinfection' describes the required validation of the effectiveness of cleaning measures in accordance with a specified sampling plan using suitable methods.

■ Suitable methods

Cleaning validation is a method that has been used in the pharmaceutical industry for decades since pharmaceutical products are often manufactured in batch processes. After a batch of an active ingredient is sent to further processing, the production equipment is being cleaned so that the next batch can be produced. The actual cleaning process is very strictly specified and is subsequently analytically validated, whereby a sample from the production equipment is analyzed for specific parameters. As long as none of the limit values is exceeded, the production equipment is considered to be clean and can be used again. This process is called cleaning validation.

■ Parameters

TOC (Total Organic Carbon) has become an established parameter for cleaning validation and offers many advantages over single substance analysis:

TOC determination is fast and straightforward. It can be carried out within a few minutes. It does not requires lengthy sample preparation. Furthermore, TOC analysis not only detects a single substance but a multitude of components and is, therefore, product-independent and highly flexible, provided that the product contains organic compounds.

Foods are generally not considered to be pure substances, as they contain different organic compounds such as carbohydrates, fats or proteins. Next to the actual product, TOC analysis also detects surfactants that are used for cleaning.

■ Sampling

Swab method: Direct sampling is carried out using the swab test. This involves careful wiping of a defined, accurately measured surface of the production equipment using a swab. The swab is subsequently extracted in a vial containing ultrapure water. The extract is analyzed for its TOC content. In swab analysis, the results are usually expressed in mg/cm^2.

The advantage of the swab method is the very accurate examination of small and particularly critical areas.

However, TOC determination via the swab method is more time-consuming and is only used for smaller parts of the entire production system.

Final-rinse method: In indirect sampling, a final rinse with water is carried out after cleaning. This final rinse water is subsequently analyzed. The advantage of the final-rinse method clearly is its speed. All that is needed is bottling and analyzing of the final rinse water.

In practice, a combination of the swab method and the final-rinse method is generally used in cleaning validation. This way, the entire production system as well as specific critical areas can be examined.

■ Measurement parameters

Measurement type: NPOC
Addition of acid: 1.5%
Sparge time: 5 minutes
Injection volume.: 50 µL

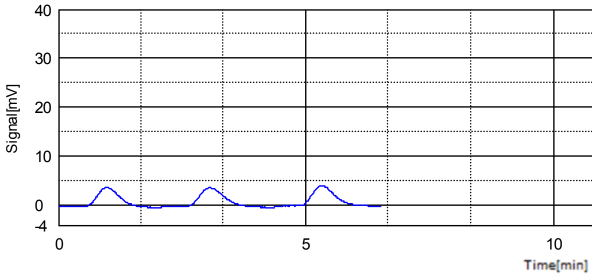

Figure: 3 Injections of the final rinse.

The NPOC content of the final rinse is 3 mg/L. The TOC limit value for cleaning validation of the production system is 10 mg/L. The cleaning efficiency was therefore verified.

■ Recommended analyzer / configuration

$TOC\text{-}L_{CXH}$ or $TOC\text{-}V_{WP}$
ASI-L / ASI-V

Application News

No. SCA-130-408

Sum parameters – Total Organic Carbon

TN_b Determination

For the risk assessment of allergen carryover in food production

The German Allergy and Asthma Association (DAAB) estimates the number of food allergy sufferers needing treatment to be around six million. While in children and infants, cow milk, soy, wheat, peanuts and hazelnuts are the main trigger, adolescents and adults generally react more strongly to raw vegetables and fruits, nuts, fish, shellfish and molluscs. Persons with food allergies are sensitive to certain food ingredients, so-called allergens.

To provide information on the consumption of allergen-containing foods to those persons affected, the 14 most frequent food allergy triggers (for example mustard, eggs, celery, peanuts etc.) are subject to appropriate package labelling. If a food contains one of these ingredients, this must be clearly indicated on the packaging. During food production or processing, traces of allergens can inadvertently get into foods via preliminary or intermediate products, without being labelled on the packaging as an ingredient.

To avoid such cross-contamination, many food manufacturers rely on cleaning validation.

▪ TN_b / TOC - Determination

Cleaning validation results can also be used to estimate a possible allergen contamination. This is performed via a 'worst case' scenario that assumes that all organic substances are allergens.

As allergens present in foods are almost exclusively proteins containing nitrogen atoms, the TN_b parameter provides considerably more information for the assessment of allergen carryover in a 'worst case' scenario than the TOC parameter alone.

TOC-L combustion analyzer with autosampler for TOC and TN_b determination

▪ Tests with foods containing allergens

Contaminated rinse water samples, i.e. with defined concentrations of an allergen-containing raw material or a product, were prepared in tap water on an experimental basis. Subsequently, these samples were analyzed for their TOC and TN_b content.

As expected, it was concluded that both the TOC and the TN_b concentrations increase linearly with increasing product concentration.

While a TOC value from an unknown rinse sample could originate from innumerable compounds such as carbohydrates, fats, surfactants etc., the TN_b parameter provides significantly more selective information on the presence of proteins. This allows for a worst-case scenario assessment with respect to allergens contained in the final rinse with respect to medical reference dosages. This calculation ensures that no relevant amounts of allergens can be carried over to subsequent production. The assessment obtained here is intended to exclude allergen carryover within a food production plant and to confirm cleaning validation. In addition, the method cuts costs because complex allergen testing is avoided.

Moreover, this type of measurement provides an objective, analytically valid measurement result, which is suitable as a basis for the assessment of consumer risks in order to ensure that the cleaning process safeguards consumer protection. Thus, if a product label contains the following information: ‘May contain traces of allergen XY’, this constitutes a quantified assessment of the allergy risk and does not merely provide precautionary information for reasons of liability.

Conclusion

A worst-case scenario is useful in assessing possible contamination by allergens, helping to ensure food safety and, consequently, protection of affected consumers.

Recommended analyzer / configuration

TOC-L $_{CPX}$

TNM-L

ASI-L

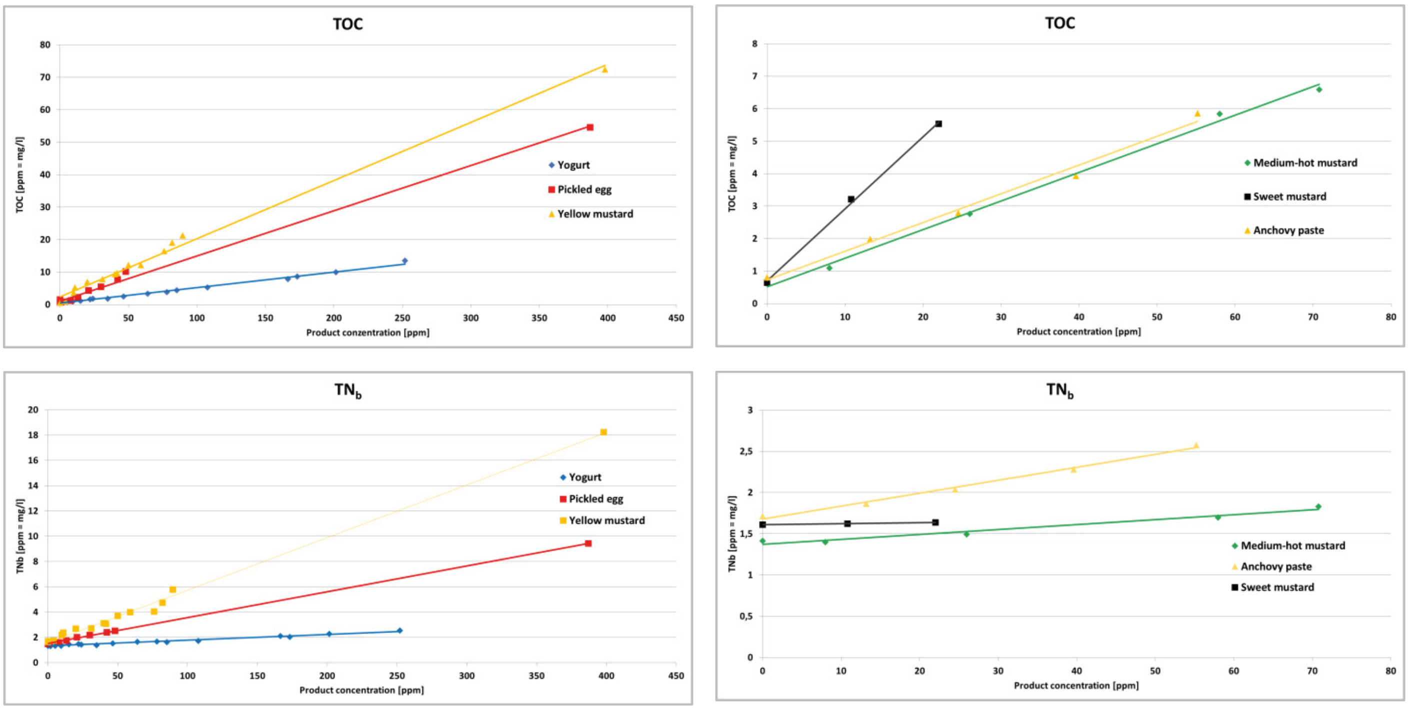

Fig.: „TOC and TN_b-calibrations“ of different foods in various concentrations

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5. TOC in daily practice

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 development 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.’

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Application News

No. SCA-130-501

Sum parameter – Total Organic Carbon

TOC – Determination methods according to EN 1484

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.

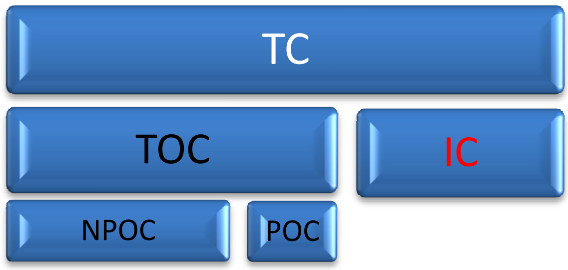
TIC: Total inorganic carbon – the sum of carbon present in water, consisting of elemental carbon, carbon monoxide, carbon dioxide (also carbonates and hydrogen carbonates), cyanide, cyanate, and thiocyanate. TOC instruments mainly detect CO_2, originating from hydrogen carbonates and carbonates, just 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.

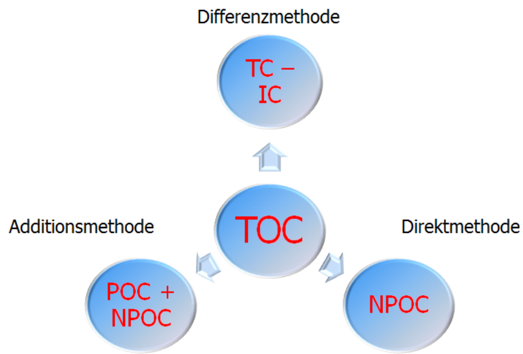
NPOC: Non Purgeable Organic Carbon – the TOC content that is not purgeable under the conditions of this method.

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 ≥ TIC).

Example:

TC – Value = 100 mg/l (RSD = 2%) ± 2 mg/l (98 – 102 mg/l)
IC – Value = 98 mg/l (RSD= 2%) ± 1,96 mg/l (96,04 – 99,96mg/l)

TOC = 2 mg/l ± 3,96mg/l (- 1,96 - 5,96 mg/l)

Due to error propagation, the total error is ± 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_2. 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_2 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_2 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_2 and detected via NDIR detector.

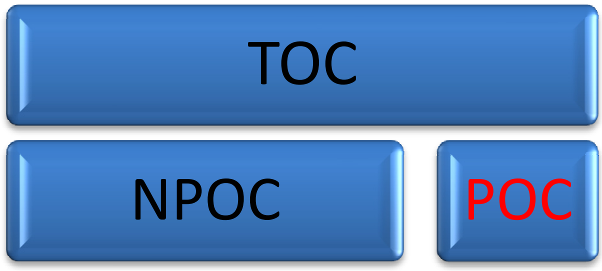


Fig. The addition method (NPOC + POC)

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_2 and transferred to the NDIR detector using a carrier gas.

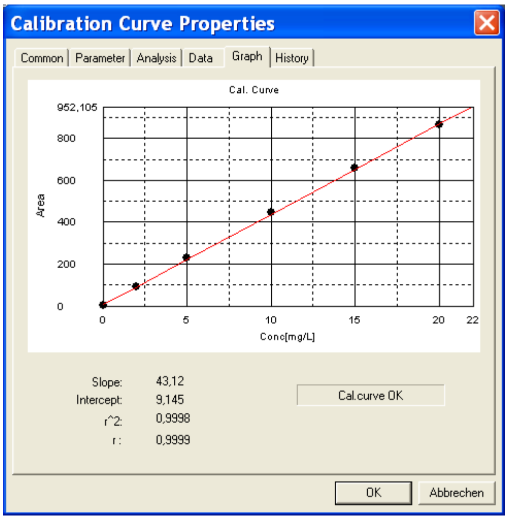
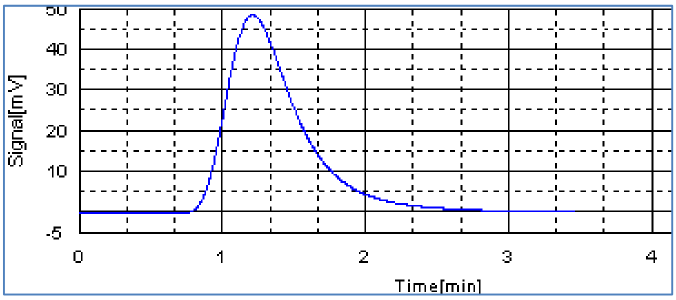
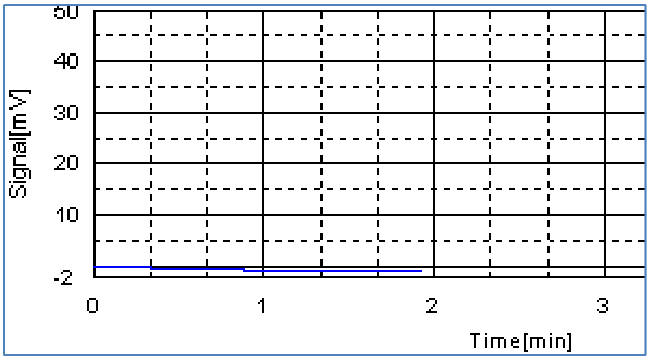


Fig. POC-Calibration with IC-standard

POC-Peak:



NPOC-Peak:



■ 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_2 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

Result:

TOC=4,05mg/l

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

NPOC=0mg/l

■ Recommended Analyzer / Configuration

$TOC\text{-}L_{CXX}$
ASI-L
POC-Option

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Application News

No. SCA-130-503

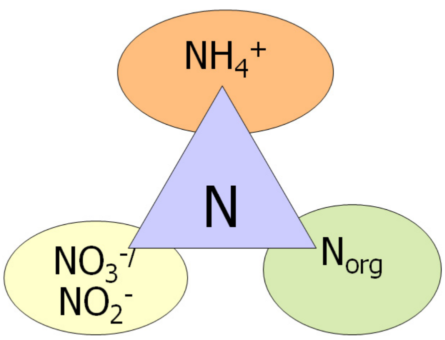
Sum parameter – Total Organic Carbon

TN_b – total bound nitrogen

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.

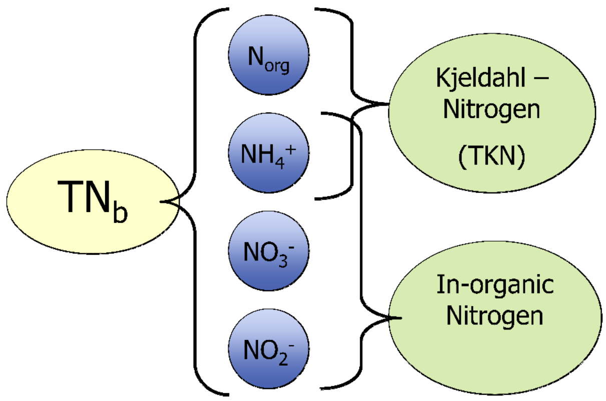
Bound nitrogen occurs in nearly all waters, mostly in the form of ammonia, nitrate, nitrite or organic compounds.



■ Total nitrogen TN_b

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_b (total bound nitrogen) was defined and standardized.

The TN_b is the total nitrogen content of a sample in the form of ammonium, nitrite, nitrate, as well as organic compounds. The TN_b does not include dissolved or gaseous nitrogen (N_2). 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_2*). In the subsequent reaction to NO_2, 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_b 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_2 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).

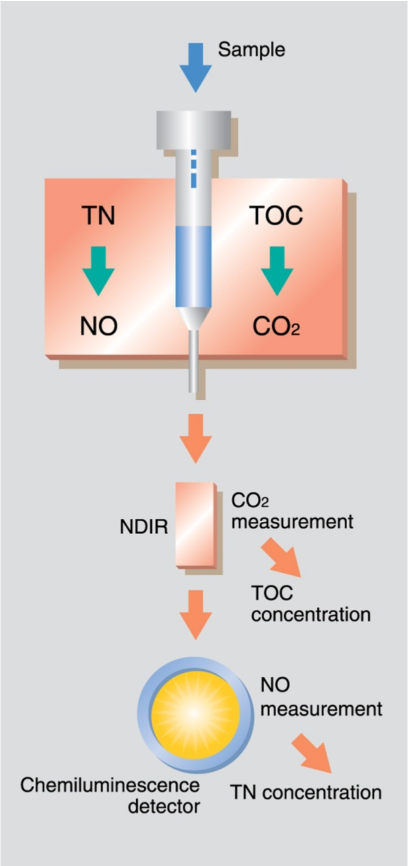


Fig. Simultaneous TOC/TN-Determination

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

■ Recommended Analyzer / Configuration

TOC-L $_{CXX}$ with TNM-L
ASI-L

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Application News

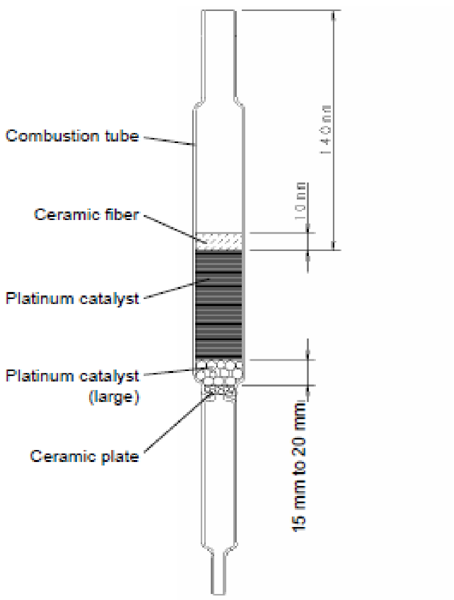
Sum parameter – Total Organic Carbon

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_2 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_2SO_4 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_2SO_4	888°C
$MgCl_2$	708°C
$CaCl_2$	782°C
K_2SO_4	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 µL.

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

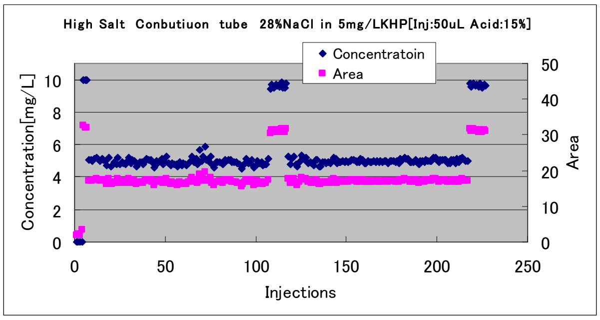


Fig. Results of endurance test

■ **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.)

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Application News

Sum parameter – Total Organic Carbon

Kit for small sample volumes

No. SCA-130-505

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)

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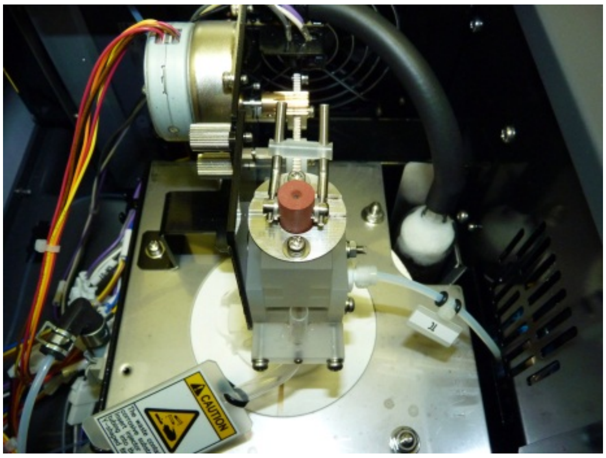
Application News

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 µL syringe. This is interesting for applications where only a very small sample volume is available.

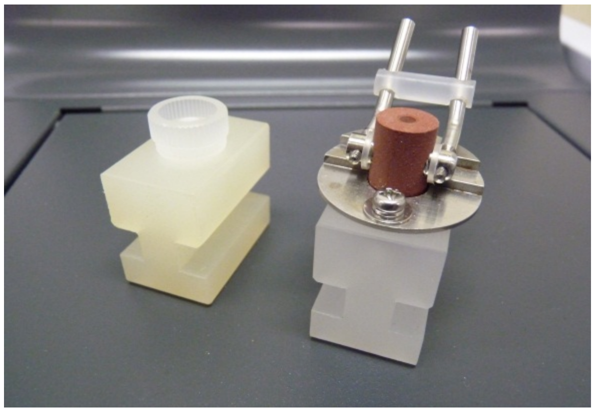


The kit for small sample volumes is a module for TOC analyzers that can be used for automated sample preparation and analysis of small sample amounts. The methods can be optimized in such a way that only a few mL of the sample are required. Optimization should, however, not be at the expense of the intermediate 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 CO or CH_4) and 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:	150µl maximal
Measurement time:	TC, IC: 3 minutes
Reproducibility:	RSD: 2%
	(over 8.000mg/L: 3%)

For gas samples:

Measurement range:	6ppm to 100% CO_2
Injection volume:	20µl bis 10mL
Measurement time:	2 – 4 Minuten
Reproducibility:	RSD: 2%

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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.

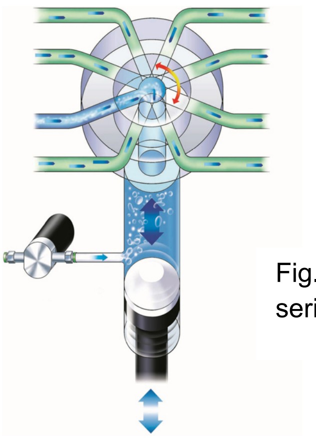
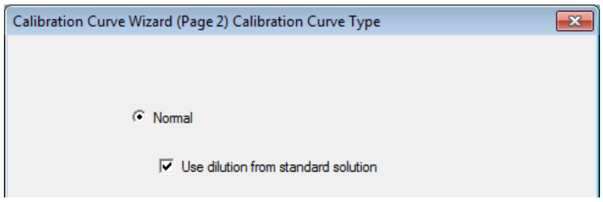


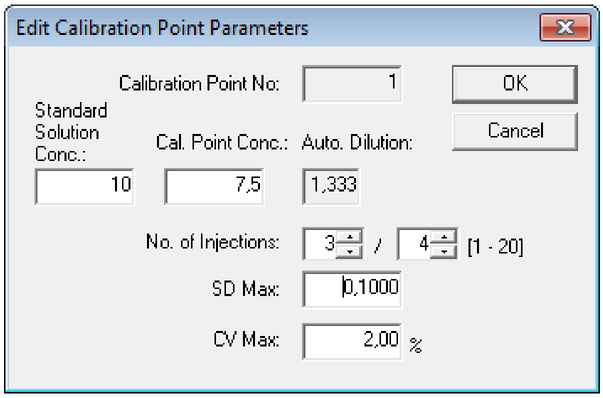
Fig. ISP-Module of TOC-L series

■ Calibration with automatic dilution function

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

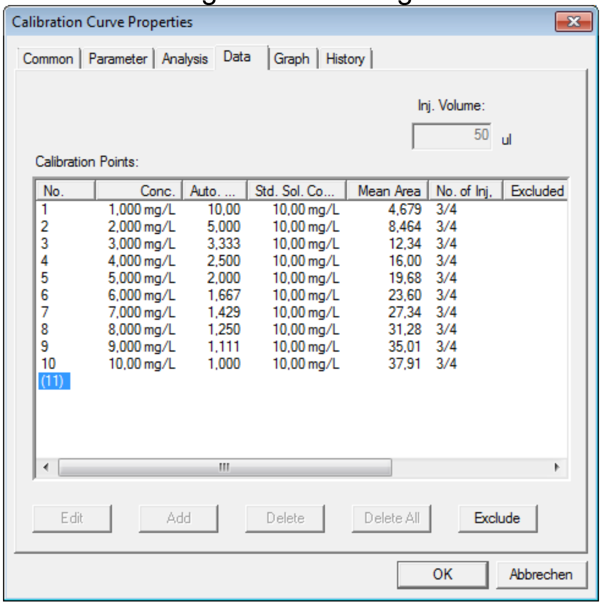


When filling the data of the calibration points, the concentration of the standard solution (stock) is entered first, followed by the desired calibration curve point. The software calculates the required dilution factor:



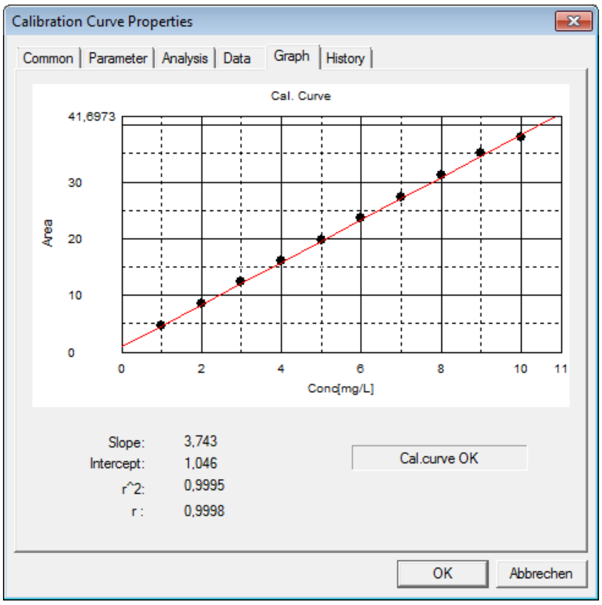
Since fractional factors are allowed, it is possible to create a 10-point calibration curve with equidistant concentration intervals from one standard solution.

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



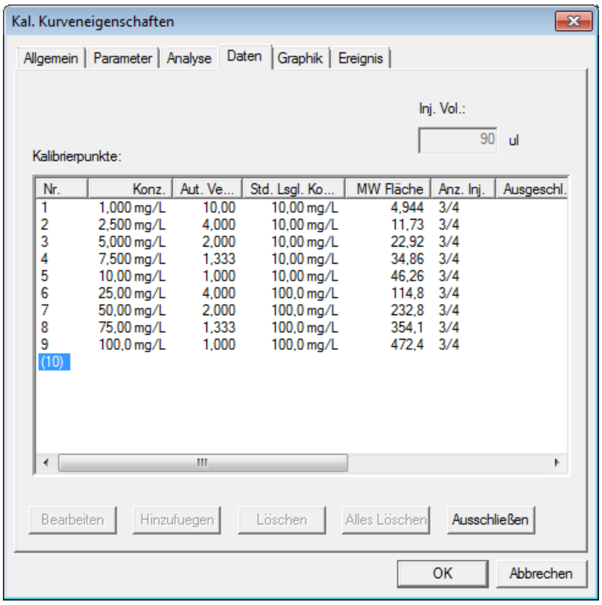
No.	Conc.	Auto. ...	Std. Sol. Co...	Mean Area	No. of Inj.	Excluded
1	1,000 mg/L	10,00	10,00 mg/L	4,679	3/4	
2	2,000 mg/L	5,000	10,00 mg/L	8,464	3/4	
3	3,000 mg/L	3,333	10,00 mg/L	12,34	3/4	
4	4,000 mg/L	2,500	10,00 mg/L	16,00	3/4	
5	5,000 mg/L	2,000	10,00 mg/L	19,68	3/4	
6	6,000 mg/L	1,667	10,00 mg/L	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	
(11)						

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



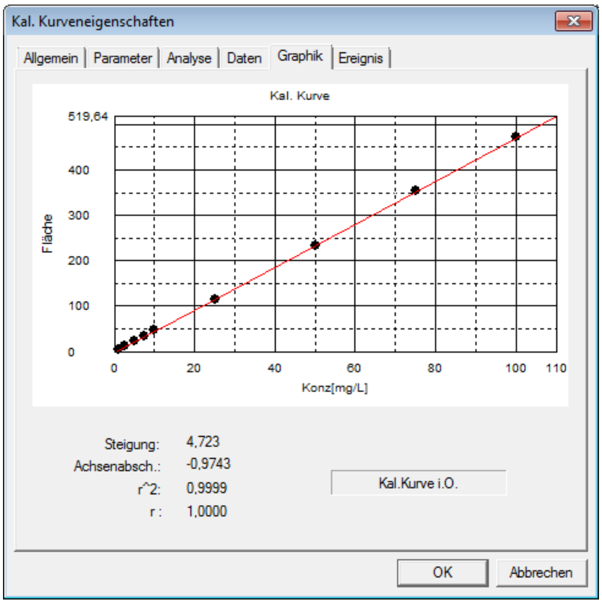
■ Calibration with automatic dilution function over two decades

In addition, there is the possibility to use different standard solution**s** 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	
(10)						

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



Application News

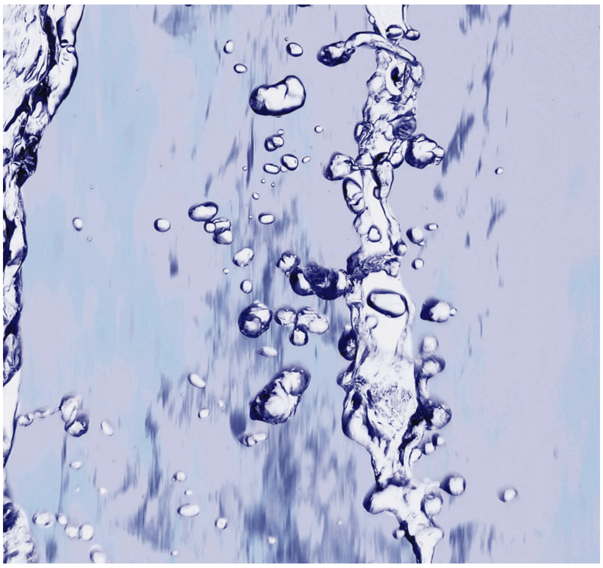
Sum parameter – Total Organic Carbon

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.

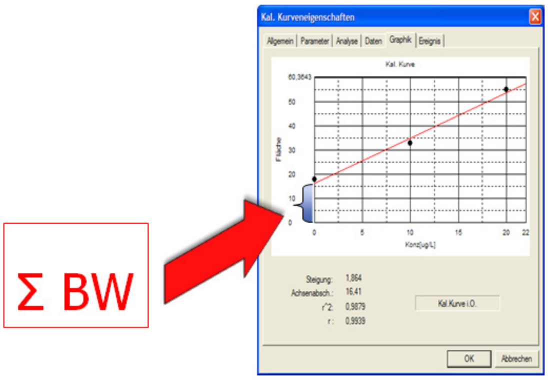
Purified waters that have been produced using highly complex water treatment systems, have different water grades. The DIN ISO 3696 standard specifies the requirements and test methods for water for analytical use and classifies these waters according to 3 grades.

Parameter	*Pure water Typ III*	*Pure water Typ II*	*Ultra pure water Typ I*
Ions, resistance (MΩ.cm)	>0,05	>1,0	>18,0
Ions, resistance (µS/cm)	< 20	<1,0	<0,055
Organix, TOC (ppb)	**<200**	**<50**	**<10**
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 = Σ 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.)

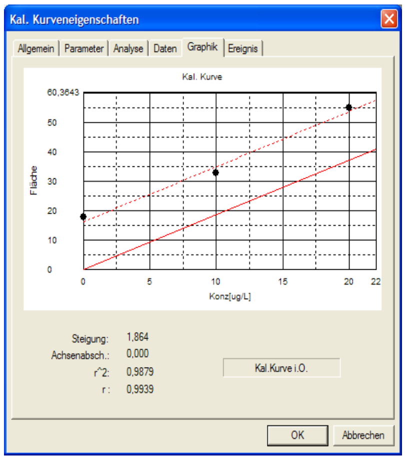
The calibration is evaluated according to the general straight-line equation:

$y = m \cdot x + b$

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.



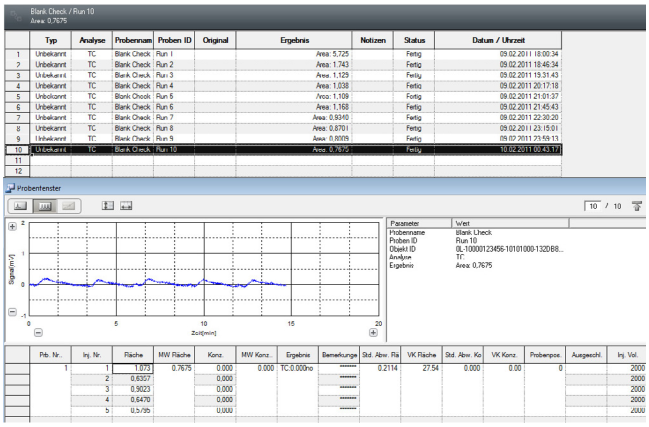
While the concentration in ultrapure water for the preparation of standard includes a blank value, the carbon concentration in an ultrapure water sample only reflects the actual TOC concentration of the sample.

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_2.

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Application News

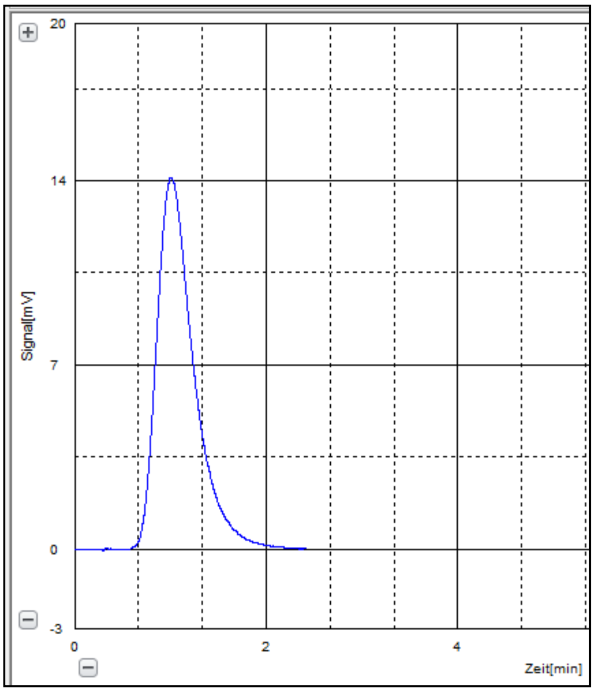
No. SCA-130-509

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_2) is cooled and dehumidified and passed through a halogen scrubber into the cell of the NDIR (Non Dispersive Infrared) detector where the CO_2 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_2 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_2SO_4	888 °C
$MgCl_2$	782°C
$CaCl_2$	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-Phenan-throline	50.0	49.7	99.4
Catechin	50.0	49.1	98.2
1,4-Benzo-quinone	100.0	100.4	100.4
Sodium acetate	100.0	98.3	98.3
Nicotin-amide	200.0	198.9	99,5
Nicotin-amide	100.0	101.3	101.3
Nicotin-amide	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
Acryl-amide	8.36	8.61	103.0
Pyridine hydro-chloride	200.0	197.1	98.6
Pyridine hydro-chloride	2.000	1.983	99.2
Quinine hydro-chloric	200.0	202.3	100.4
Quinine hydro-chloric	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!

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Application News

No. SCA-130-510

Sum parameter – Total Organic Carbon

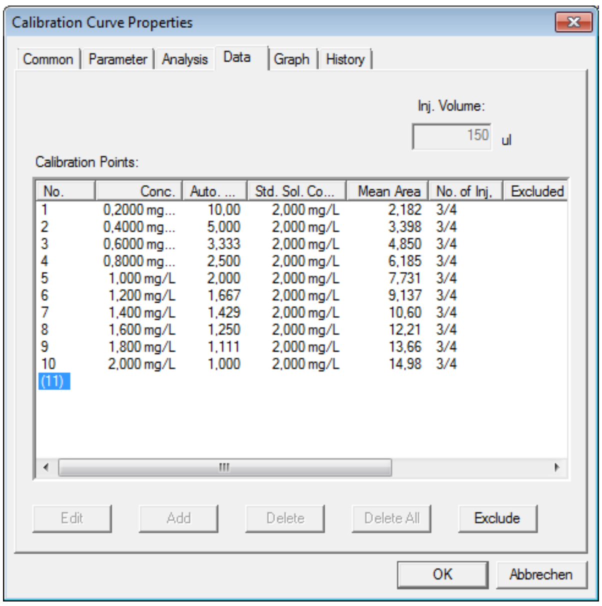
Detection and determination limit of NPOC method with standard catalyst

■ Measurement parameters

System:	TOC-L CPN
Catalyst:	Standard catalyst (Al-balls covered with Pt)
Method:	NPOC (removing of IC by acidification and sparging)
Acidification:	1,5%
Sparge time:	2 min
Injection vol.:	150µl

■ Calibration with automatic dilution function

A 10 point calibration curve is carried out by using the automatic dilution of a 2mg/L C stock solution.


Calibration Curve Properties

Common | Parameter | Analysis | Data | Graph | History

Inj. Volume: 150 ul

Calibration Points:

No.	Conc.	Auto. ...	Std. Sol. Co...	Mean Area	No. of Inj.	Excluded
1	0,2000 mg...	10,00	2,000 mg/L	2,182	3/4	
2	0,4000 mg...	5,000	2,000 mg/L	3,398	3/4	
3	0,6000 mg...	3,333	2,000 mg/L	4,850	3/4	
4	0,8000 mg...	2,500	2,000 mg/L	6,185	3/4	
5	1,000 mg/L	2,000	2,000 mg/L	7,731	3/4	
6	1,200 mg/L	1,667	2,000 mg/L	9,137	3/4	
7	1,400 mg/L	1,429	2,000 mg/L	10,60	3/4	
8	1,600 mg/L	1,250	2,000 mg/L	12,21	3/4	
9	1,800 mg/L	1,111	2,000 mg/L	13,66	3/4	
10	2,000 mg/L	1,000	2,000 mg/L	14,98	3/4	
(11)						

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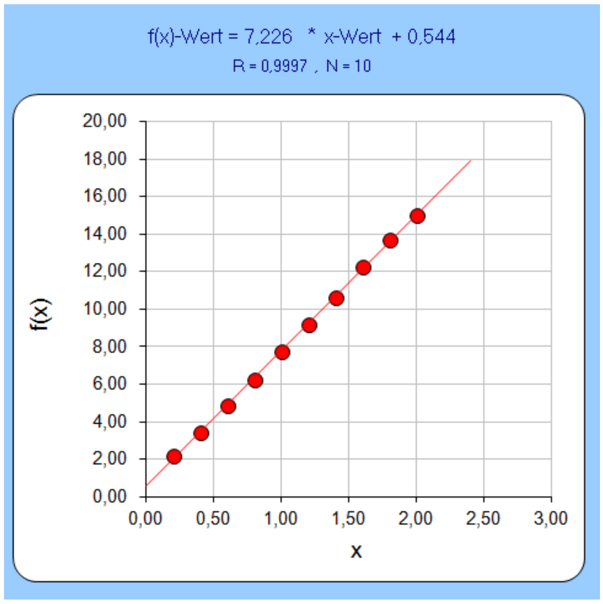
■ Calculation of detection and determination limit according to DIN 32645



Characteristics

Slope a:	7,226
Intercept b:	0,544
Correlation coefficient r:	0,9997
Result uncertainty:	33,3%
Probability of error (a):	5,00%
Number of measurements n:	3
Standard error of estimate Sy:	0,108
Standard error of procedure Sx:	0,015
Sum of squared deviations:	3,3
Quantile (one-sided):	1,860
Quantile (two-sided):	2,306

Limit of detection: 0,025mg/L
Limit of quantification: 0,089mg/L

Note: The results depend on the selected injection volume, the purity of the vessels, water, chemicals and gases used.

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Application News

No. SCA-130-511

Sum parameter – Total Organic Carbon

TOC determination with wet chemical UV-oxidation

Two oxidation techniques are now commonly used in TOC analysis: catalytic combustion and wet-chemical oxidation.
In catalytic combustion, carbon compounds are converted to CO_2 using high temperatures and a catalyst, with subsequent detection of the resulting CO_2 using an NDIR detector.
Wet-chemical oxidation uses a combination of UV irradiation and persulfate oxidation.

■ Wet chemical UV-oxidation

In the wet chemical UV-oxidation, the oxidation power of OH-radicals is used.
T
he UV (185nm) activates the H2O to generate the [OH•] radicals as
H_2O + hv (185nm) $\rightarrow OH\bullet + H^+$

The UV (185nm) also activates the persulfate to generate the [OH•] radicals as
$S_2O_8^{2-}$ + hv (254nm) $\rightarrow$ 2 SO_4^-
$SO_4^- + H_2O \rightarrow HSO_4^- + OH\bullet$

OH radicals are strong oxidants and oxidize the carbon compounds to CO_2.

{Organic compounds} + OH • $\rightarrow$ $CO_2 + H_2O$

In addition the temperature has an influence to the oxidation reaction. The following figure illustrates the influence of the different parameter:

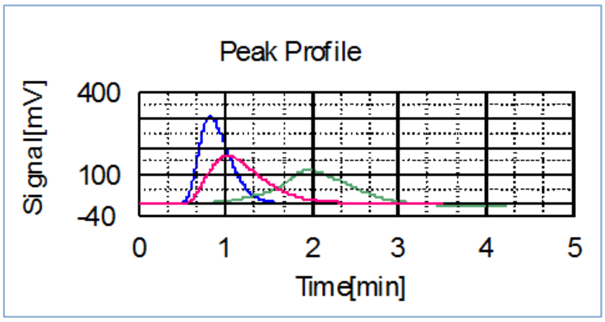

Abb.: Peak graph of KHP standard (NPOC = 5 mg/l)

Blue: Temperature / UV / Persulfate
Peak shape : 2.46 min.

Red: UV / Persulfate
(Peak shape: 3.54 min.)

Green: Temperature / Persulfate
(Peak shape: 4.13 min.)

The graph shows signal vs time for the analysis of a 5 ppm KHP standard using the different methods. The graph clearly demonstrates that the combined method of UV, persulphate and temperature has the shortest analysis time and sharpest peak shape.

■ TOC-V $_{WP}$

The key technique of the TOC-VWP analyzer is the powerful oxidation via the combination of sodium persulphate and UV oxidation at 80 °C. A persulphate solution is needed for the determination and it is therefore important that this solution does not contain any contaminants that could negatively affect the measuring value.

The TOC-V_{WP} contains an automatic reagent preparation function that eliminates possible contamination of the persulphate solution in order to assure that the average TOC value truly originates from the sample – and not from the reagent solution used.

The sample is added to the persulphate solution in the TC reactor, which is heated under UV illumination to convert the carbon content to carbon dioxide.

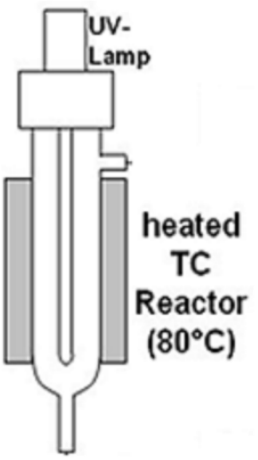

Figure.: TC reactor with integrated UV lamp and heating

■ Advantage of the method

In the combustion oxidation the injection volume is limited to 2000µl (because of the pressure impulse after injection). The wet chemical oxidation can use injection volume up to 20400µl. This high injection volume leads to higher sensitivity and therefore enables high precision measurements in the lower ppb range.
The detection limit of these systems is 0,5µg/L.

■ Limitations

The wet chemical oxidation detects less particles. To measure samples containing particles the catalytic combustion with its higher oxidation potential has to be used.
In addition, simultaneous TOC/TN_b measurements can be carried out.

■ Application

The main domain of the wet chemical oxidation is the analyses of ultra pure water (pharma water, semiconductor industry, condensate…), because of the low detection and good reproducibility in the ppb range.
Or in special applications, where the combustion technique is not suitable.

Example of applications

- 205 TOC determination in ultra pure water with wet chemical oxidation
- 309 TOC determination in phosphoric acid (TOC-V WP)

Figue: TOC-V $_{WP}$ with ASI-V

■ Recommended analyzer / Configuration

TOC-$V_{WP/WS}$
ASI-V (with 40ml or 125ml vials)

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Application News

No. SCA-130-512

Sum parameter – Total Organic Carbon

Silanisation of the syringe – TOC-determination of surfactants

The TOC determination of a surfactant solution was not reproducible, nor did they correspond with the theoretically calculated values. Subsequently, TOC direct determination of the surfactant was executed using the solid sampler SSM. The measurement values obtained this way corresponded well with the theoretical values. This led to the conclusion that conversion of carbon to CO_2 was not the problem, rather that the surfactant exhibits interactions with the glass surface. Consequently, carbon is being removed from the surfactant solution, which explains the lower TOC measurement values.

The main module of the TOC-L CPH is the ISP module (integrated sample preparation system). It consists of an 8-port valve and a syringe with sparging connection. The syringe is made of glass. In order to prevent interaction of the surfactant with the glass surface, the syringe is first silanized.

■ Required material for silanisation

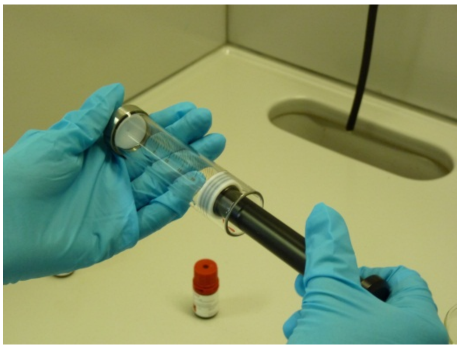
- 1ml N-Methyl-N-(trimethylsilyl)trifluoro-acetamide (for GC derivatization, ≥98.5%) – e. g.: von Fluka, No. 69479)
- approx. 20ml methanol
- 1ml syringe with needle

■Preparation and security notes

First the syringe has to be clean and dry. Please refer to the warning remarks of the used chemicals, wear protective clothing and work under the extractor hood.

■ Procedure

- Take the silanization reagent (1ml) and put it into the syringe
- Turn the syringe 5 – 10 minutes to coat the complete surface



- Drain the silanisation reagent
- Remove the excess MSTFA by washing two times with 10ml methanol.
- Following this procedure, the syringe is rinsed with water and dried (at 40°C - 50°C in the dying cabernet)
- After 24 hours, the syringe is ready for use

■ Note

It is difficult to assume about the long-term stability of this silanization. It depends of different influences.

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Application News

No. SCA-130-513

Sum parameter – Total Organic Carbon

TOC determination with solid module SSM-5000A

In addition to aqueous samples, TOC determination can also performed on soil, sludge, sedimentation and other solid samples. By swabbing, the carbon in attached residues can be measured for cleaning validation.

In some regulation (e.g regulation for the acceptance of waste at landfills pursuant) a limit value for TOC is mentioned.

The modular design of Shimadzu's TOC series supports straightforward combination with a solid sample module. In this way, the instruments can also be employed for the analysis of solids. The SSM-5000A module can be used in combination with TOC-L a TOC-V wet-chemical.

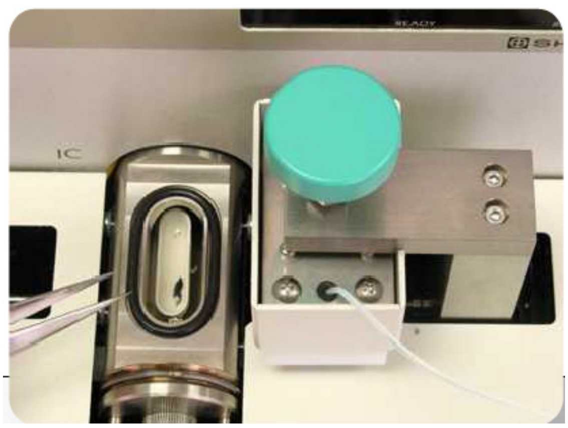
The solid module allows the separate determination of TC (Total carbon) and the IC (inorganic carbon). It has two different sampling parts.
The module is fully integrated into the TOC software (standalone and TOC-Control software) which automatically calculates the TOC-content.

■ TC – Determination
For the TC determination, a subsample of the dried solids is weighed into a ceramic boat and combusted at 900 °C in a stream of oxygen. To ensure complete conversion to CO_2, the generated gases are passed over a mixed catalyst (cobalt/platinum) for catalytic post-combustion. The CO2 produced is subsequently transferred to the detector in the main unit.

The SSM-5000A solid sample module does not have its own detector, but is coupled to the NDIR detector of the main instrument (TOC-V or TOC-L).

The NDIR detector of the main unit contains a tandem cell consisting of a long cell and a short cell the long cell is used for water analysis and a short cell for solid sample analysis.
This configuration assures that the system can be employed for measurements of solids, while retaining its complete flexibility and switching functionality between water and solid sample analysis without any additional conversion.

■ IC – Determination
The determination of the inorganic carbon is carried out in a separate furnace of the module. Phosphoric acid is added to the sample and the resulting CO_2 is purged at 200 °C and measured.



■ Calibration

The SSM calibration can be carried out at different manner. A solid (with known C-content) is weight in a ceramic boat or a standard solution is added to a sample boat filled with ceramic wool.

In case of solid calibration, different weights in of one compound (for example glucose) are used. Based on the carbon content of the compound (Glucose contains 40% carbon) the absolute carbon content in the boat is calculated (in µg) and used for the calibration graph (x-axis).

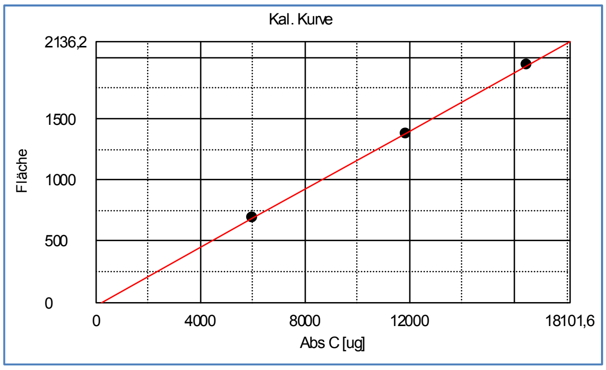


Figure: TC-Calibration with Glucose

The IC calibration can be done with sodium hydrogen carbonate (for instant).

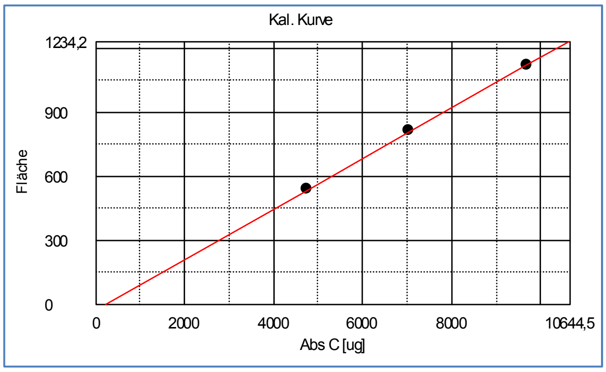
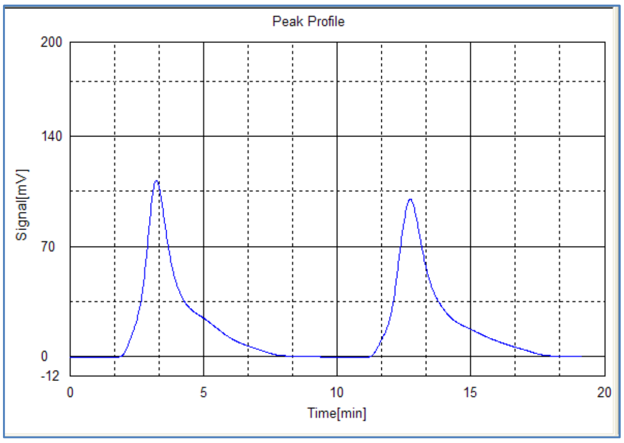


Figure: IC-Calibration with $NaHCO_3$

■ Example of a real solid sample (Bauxit)

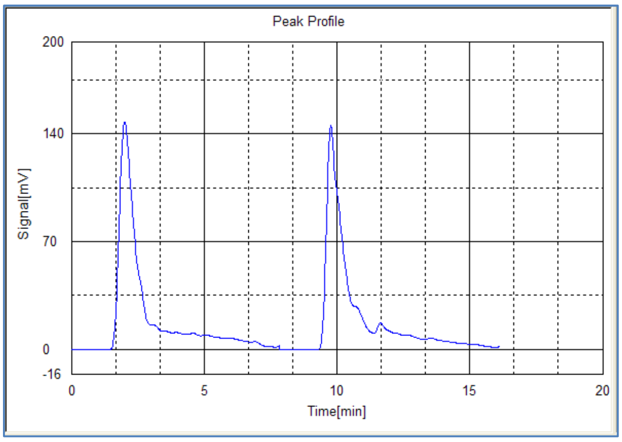
TC determination

Result: 1.30 ± 0.001% (CV: 0,11%)



IC determination

Result: 0,94 ± 0.009% (CV: 0,95%)



TOC-Result: 0,36%

■Recommended analyzer / Configuration

TOC-L or TOC-V wet chemical

SSM-5000A

Example of Application

108 TOC determination in solids

203 TOC determination in cleaning validation – SWAB method

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Application News

No. SCA-130-514

Sum parameter – Total Organic Carbon

Comparison of different sum parameters – COD, BOD and TOC

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

■ BOD (Biochemical Oxygen Demand)

The BOD value indicates the amount of oxygen in water needed for biological decomposition of organic compounds dissolved in wastewater. For BOD determination, microorganisms are added to the water sample. After a predefined time interval, usually five days, the oxygen consumed by bacteria during decomposition of organic compounds in the water sample is determined. The BOD5 test is much too slow to provide suitable information and the results obtained are therefore not useful for monitoring and controlling of wastewater treatment procedures. For continuously operated BOD analyzers, determination within 5 -15 minutes has been attempted.

■ COD (Chemical Oxygen Demand)

The COD value indicates the amount of oxygen needed to chemically oxidize organic compounds present in wastewater. A chemical oxidizing agent is added to the sample and its consumption is subsequently measured. In addition to the organic compounds, other compounds (nitrites, bromides, iodides, metal ions and sulfur compounds) present in the water sample can also be oxidized and have an influence on the measuring value.

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

■ TOD (Total Oxygen Demand)

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

■TOC, total organic carbon

The TOC content is a measure of the concentration of organically bound carbon and is therefore a direct indication of the pollution levels by organic compounds in wastewater. For TOC determination, the sample is typically first acidified in order to convert the inorganic carbonate and hydrogen carbonate compounds into carbon dioxide. The dissolved CO_2 is subsequently removed from the sample via sparging with a stream of carrier gas. The remaining organic carbon compounds are then converted to CO_2 via high temperature (catalyst) or wet-chemical oxidation. The amount of CO_2 obtained is subsequently determined via NDIR detection. NDIR is a specific detection mode that renders TOC determination free from the effects described above when using other parameters. Based on this, the TOC parameter is used in many environmental regulations. Another advantage is the relatively simple conversion of TOC measurements into a continuous monitoring procedure.

■ Correlation between COD and TOC

In recent years, COD measurements are increasingly being replaced by TOC analysis. However, as the threshold values for organic pollution levels in wastewater are usually described and determined as COD values, efforts are underway to find a correlation between the two parameters.

For single compounds the factor can be calculated.

1. Example Glucose ($C_6H1_2O_6$) 1000mg/L
COD= 1067mg/L
TOC= 400mg/L
Correlation COD/TOC= 2,66

2. Example Acetone (C_3H_6O) 1000mg/L
COD=2207mg/L
TOC= 621mg/L
Correlation COD/TOC= 3,55

3. Example Ethanol (C_2H_6O) 1000mg/L
COD=2087mg/L
TOC= 522mg/L
Correlation COD/TOC= 4,00

The examples show the diversity of correlation factors. In addition to the organic compounds, other compounds like nitrites, bromides, iodides, metal ions or sulfur compounds may be oxidized and influenced the factor.
Due to this, the correlation factor can be vary between 2,5 and 4 depending of the wastewater.

In order to simplify the determination of the correlation factor, paragraph 6 of the German wastewater law (AbwV) of June 17, 2004 includes the following: “One of the values for the chemical oxygen demand (COD) as defined in the wastewater regulatory law is, under compliance with paragraph 1, also valid when the four-fold value of the total organically bound carbon (TOC) in mg/L, does not exceed this value”.

In the European Union, the factor „3“ is used for conversion of TOC in COD.

The instrument software of Shimadzu TOC systems (TOC-L standalone, TOC-Control L, TOC-4200 standalone) enables the automatic conversion of measured TOC values into COD value (if the correlation is known).

Application News

No. SCA-130-515

Sum parameter – Total Organic Carbon

COD and TOC correlation factor – Conversion examples

The determination of the chemical oxygen demand (COD) is time-consuming and complex. After the sample has been mixed with various reagents, it is left to boil at 120°C (according to DIN regulation) under reflux (air cooler), subsequently an aliquot of the mixture is back-titrated or photometrically measured (rapid test).
In addition, environmentally hazardous substances, such as a mercury-containing sulfuric acid and a potassium-dichromate solution are used.

The determination of TOC (Total Organic Carbon), on the other hand, is fast and easy to perform. In addition, less than 1 mL of a diluted hydrochloric acid solution is used for each analysis.

■ COD and TOC in the German Waste Water Ordinance (AbwV)

For decades, there have been efforts to replace the COD by the TOC parameter. However, to date the COD is laid down in the German Waste Water Ordinance. In order to still use the TOC parameter, Article 6 “Compliance with the requirements” of the German Waste Water Ordinance states the following:
(3) “With due regard for paragraph (1) above, a chemical oxygen demand (COD) level specified in the water discharge permit shall also be deemed to have been met provided the quadruple amount of total organically bonded carbon (TOC), specified in milligrams per liter, does not exceed this level.”

■ Theoretical COD/ TOC factor

If the TOC is used as an analytical parameter to calculate the COD, a conversion factor is required. The AbwV specifies the factor 4. A theoretical factor is derived from the reaction ratios between C and O_2:

$$\boldsymbol{C + O_2 \rightarrow CO_2}$$

As the COD corresponds to the required oxygen amount, the O_2 consumption corresponds to the COD value – C represents to the TOC value.

Since the COD or the TOC concentrations must be expressed in terms of mass concentration, the molar masses of the two reactants are used here for the conversion. The ratio of carbon concentration to oxygen concentration corresponds to the TOC/COD correlation. Based on the reaction equation above, this means

for C: $1000\frac{mg}{L} : 12\frac{g}{mol} = 83.33\frac{mmol}{L}$

for O_2: $1000\frac{mg}{L} : 32\frac{g}{mol} = 31.25\frac{mmol}{L}$

The COD factor is derived from the molar ratio of C to O_2:

$$88.33\frac{mmol}{L} : 31.25\frac{mmol}{L} = 2.667$$

In this case, the conversion from TOC to COD is as follows:

$$COD\ (O_2)\left[\left[\frac{mg}{L}\right]\right] = TOC\ \left[\left[\frac{mg}{L}\right]\right] * 2.667$$

The example above describes the oxidation of carbon with oxygen. For organic substances the ratio between carbon atoms and oxygen atoms is different, which is of direct influence on the conversion factors from TOC to COD.

Here are a few examples.

■ Oxalic acid

Oxidation of oxalic acid proceeds as follows:

$$2\,C_2H_2O_4 + O_2 \rightarrow 4\,CO_2 + 2\,H_2O$$

4 carbons react with an oxygen molecule. This is the calculation:

for C: $1000\frac{mg}{L} : (4 * 12\frac{g}{mol}) = 20.83\frac{mmol}{L}$

for O_2: $1000\frac{mg}{L} : (1 * 32\frac{g}{mol} = 31.25\frac{mmol}{L}$

$$20.83\frac{mmol}{L} : 31.25\frac{mmol}{L} = 0.667$$

■ Benzene

The way oxidation of benzene proceeds:

$$2\,C_6H_6 + 15\,O_2 \rightarrow 12\,CO_2 + 6\,H_2O$$

12 Carbons react with 15 oxygen molecules. The calculation is as follows:

for C: $1000\frac{mg}{L} : (12 * 12\frac{g}{mol}) = 6.94\frac{mmol}{L}$

for O_2: $1000\frac{mg}{L} : (15 * 32\frac{g}{mol}) = 2.08\frac{mmol}{L}$

$$6.94\frac{mmol}{L} : 2.08\frac{mmol}{L} = 3.34$$

■ Methanol

Oxidation of methanol:

$$2\,CH_3OH + 3\,O_2 \rightarrow 2\,CO_2 + 4\,H_2O$$

2 Carbons react with 3 oxygen molecules. The calculation is as follows:

for C: $1000\frac{mg}{L} : (2 * 12\frac{g}{mol}) = 41.67\frac{mmol}{L}$

for O_2: $1000\frac{mg}{L} : (3 * 32\frac{g}{mol}) = 10.42\frac{mmol}{L}$

$$41.67\frac{mmol}{L} : 10.42\frac{mmol}{L} = 4.000$$

■ Real water samples

These examples show how the COD factor can be calculated. They also illustrate why, due to the composition of a sample, the COD factor may vary so much.

In addition, real water samples usually contain a large number of different organic substances. This is why the bandwidth of the conversion factors ranges from < 1 to > 5, depending on the amount of oxygen that is already bound in the organic compounds.

Furthermore, COD determination also measures oxidizable inorganic compounds, such as nitrites, bromides, iodides, metal ions and sulfur compounds and this may influence the conversion factor.

The instrument software of Shimadzu TOC systems (TOC-L standalone, TOC-Control L, TOC-4200 standalone) enables the automatic conversion of measured TOC values into COD value (if the correlation is known).

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Application News

Sum parameters – Total Organic Carbon

TOC – Control samples and control cards

No. SCA-130-516

Analytical quality assurance is an important topic in many analytical application areas. Various information leaflets as well as appropriate quality standards provide tips or guidelines on the most suitable measures to attain high-level analytical quality.

■ Control samples

Control samples are important tools in analytical quality control. Specially prepared solutions of known concentration are used to test the system and the validity of the specific calibration. The control samples are treated like unknown samples to determine the concentrations or recovery. The user's quality management system specifies a tolerance range the target value should be in.

The TOC Control software of the TOC-L and TOC-V systems enable the definition of such control samples.

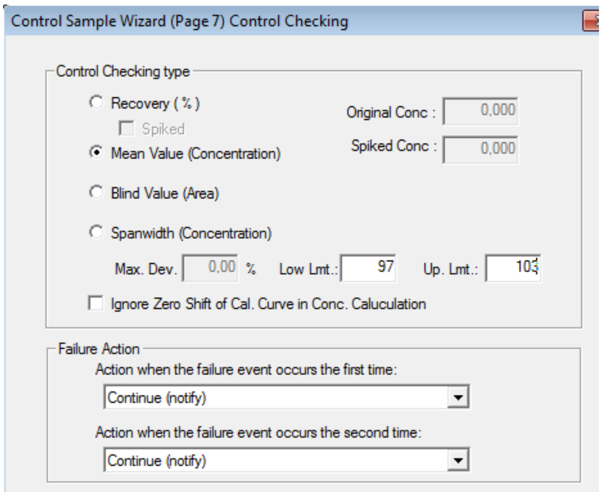


Figure: Control sample parameters.

Users can define their own parameters for each control sample. The results can be specified either in terms of concentration or directly in terms of recovery.

Blind value controls can be defined as well. The blind values are usually entered without specifying a concentration (area).

■ Measures

The TOC autosamplers often run overnight and process the samples sequentially until the next morning. All the more annoying when the analytical staff finds out the following morning that the control samples are outside of the specified tolerance limit. In such cases, the software offers a solution.

When tolerance limits are exceeded, the software can, for example, start an automatic recalibration or repeat the run of the last control sample within the tolerance limits.

When 'precious' samples need to be measured, or only very small amounts of the sample material are available, the analytical run can also be stopped.

■ Control cards

In order to identify trends or system deterioration in due time, the measurement values of the control samples are documented on a time axis. This leads to so-called control cards, in which the results are listed on the Y-axis and the corresponding dates on the X-axis.

■ **Control card program**

The TOC Control Software features an integrated control card program. This way, the user does not need to transfer values manually. This is done automatically by the system.

In the cards, control and warning limits are defined that must not be exceeded. They can be determined automatically by the program (in a so-called pre-period) or manually entered by the user.

With the software, the following control cards can be generated and applied:

- Mean value control cards
- Blind value control cards
- Recovery control cards
- Span width control cards
- Individual control cards (target value control)

An editable cell also provides the option to comment on the result entries.

■ **Recommended analyzer / Configuration**

- TOC-V / L
- TOC-Control V / L

Example of mean value control card

Pre-Period: 12 Samples
Mean value: 7,69mg/L
Control limit: 7,36mg/L and 8,02mg/L (green line)
Warning limit: 7,47mg/L and 7,91mg/L (blue line)
Out of control event: Sample 55 is over the control limit

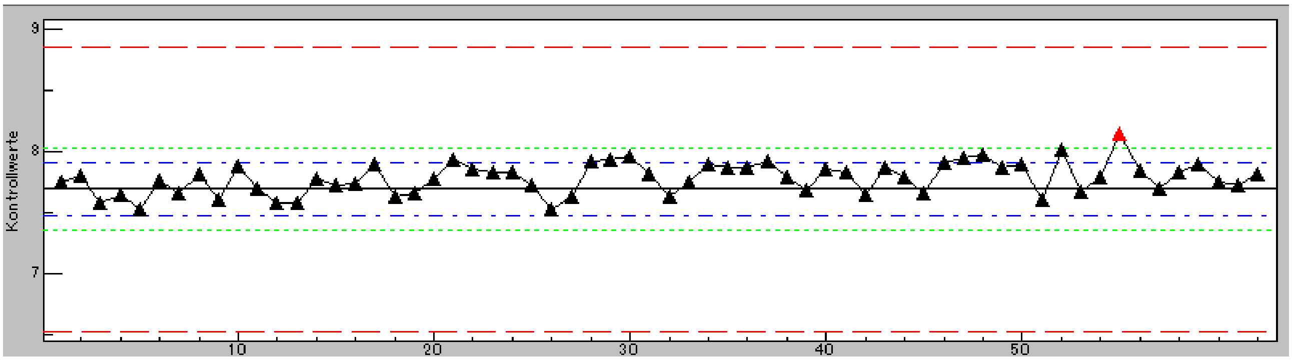


Figure: Mean value control card
Measurements that lie outside of the control limits are automatically marked.

Application News

No. SCA-130-517

Sum Parameter – Total Organic Carbon

Manual injection of low sample volumes

The manual injection kit can be used to perform TOC analysis in gases or liquids. Manual injection of liquids requires just small sample amounts. In general, the injection quantity is 50 – 150 µL. As a result, multiple injections only require sample volumes of less than 0.5 mL.

In particular, the manual injection kit is needed for the measurement of highly valuable samples, or in cases of very small sample amounts available.

To retrofit the TOC-L with the manual injection kit, the injection slider is removed and replaced by an injector block. Changing both injector blocks (TC port / IC port) takes less than a minute.

Afterwards the sample can be injected manually onto the catalyst or the IC port using conventional GC injection syringes.

As detection limit and reproducibility, among others, also depend on the injection volume, injection volumes of > 100 µL are often used.

The highly sensitive NDIR detector also permits injection of very small volumes such as 5 µL.

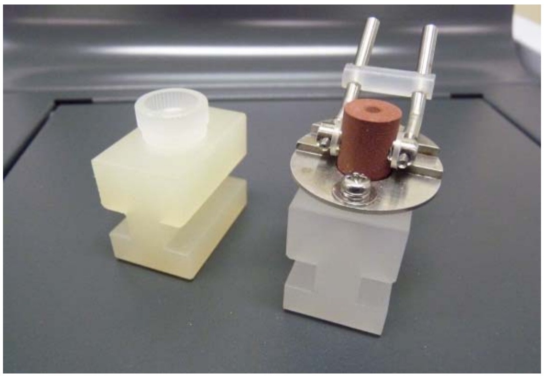


Figure: Injection blocks for manual injection (IC and TC).

■ Calibration

As an example, a TC calibration using the manual injection kit is discussed here. The measurement range of the calibration is between 2.5 mg/L and 20 mg/L C (calibration substance: potassium hydrogen phthalate).

The injection volume was 5 µL and injection for each calibration point was carried out at least twice.

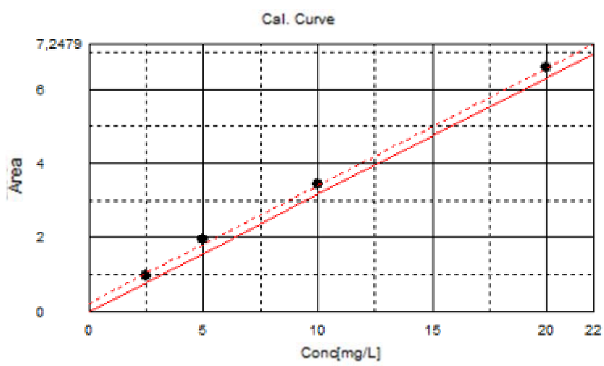


Figure: TC calibration using an injection volume of 5 µL (r = 0,9996).

■ Detection limit

The areas obtained were used to calculate the limits of detection and determination in accordance with DIN 32645.

Limit of detection: 0.772 mg/L

Limit of quantification: 2.968 mg/ L

Following calibration, a control sample with a TOC content of 15 mg/L (3 injections) was measured. The recovery was 97.4% (14.6 mg/L).

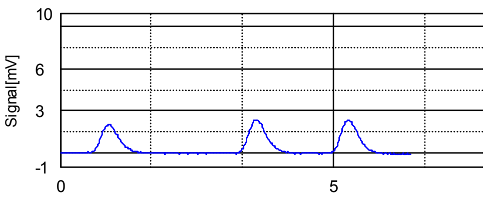


Figure: Peaks of the control sample (15 mg/L)

■ Measuring range < 1 mg/L

When limits of detection and determination are desired that are significantly lower than 1 mg/L, it is possible to increase the injection volume to 20 µL. A concentration range of 0.5 – 5.0 mg/L was selected for this purpose.

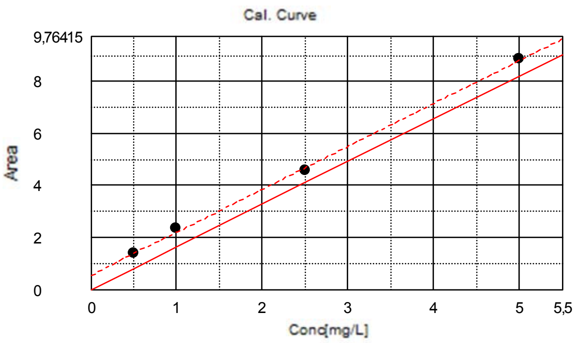


Figure: TC calibration with 20 µL injection volume (r = 0.9998).

The limits of detection and determination in this case also clearly is below 1 mg/mL.

Limit of detection: 0.249 mg/L

Limit of determination: 0,911 mg/ L

Note: The reproducibility of the method is also dependent on the injection routine of the user.

■ Recommended analyzer / configuration

TOC-L_{CXH}

Manual gas sample injection kit

Application News

No. SCA-130-518

Sum parameter – Total Organic Carbon

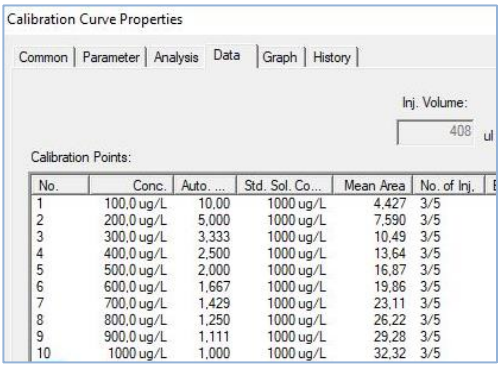
Determination of limit of detection and quantification for the NPOC method using High Sensitivity Catalyst

■ Measurement parameters

System: TOC-L CPH
Catalyst: High Sensitivity Catalyst (platinum coated wool)
Method: NPOC (IC-removal)
Acidification: 1,5%
Sparge time: 2 min
Injection vol.: 408µl

■ Calibration with automatic dilution function

A 10-point calibration curve is carried out by using the automatic dilution of a 1.000µg/L C stock solution.



Calibration Curve Properties

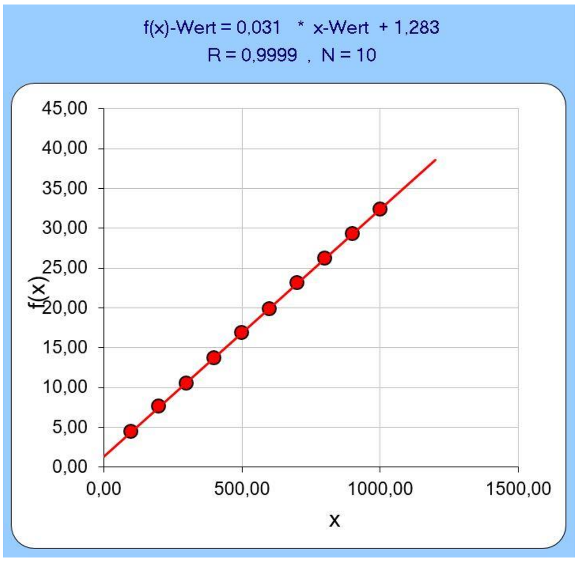
Common | Parameter | Analysis | Data | Graph | History

Inj. Volume: 408 ul

Calibration Points:

No.	Conc.	Auto. ...	Std. Sol. Co...	Mean Area	No. of Inj.
1	100,0 ug/L	10,00	1000 ug/L	4,427	3/5
2	200,0 ug/L	5,000	1000 ug/L	7,590	3/5
3	300,0 ug/L	3,333	1000 ug/L	10,49	3/5
4	400,0 ug/L	2,500	1000 ug/L	13,64	3/5
5	500,0 ug/L	2,000	1000 ug/L	16,87	3/5
6	600,0 ug/L	1,667	1000 ug/L	19,86	3/5
7	700,0 ug/L	1,429	1000 ug/L	23,11	3/5
8	800,0 ug/L	1,250	1000 ug/L	26,22	3/5
9	900,0 ug/L	1,111	1000 ug/L	29,28	3/5
10	1000 ug/L	1,000	1000 ug/L	32,32	3/5

■ Calculation of limit of detection and quantification according to DIN 32645



Characteristics

Slope a:	0,031
Intercept b:	1,283
Correlation coefficient r:	1,000
Result uncertainty:	33,3%
Probability of error (a):	5,00%
Number of injections:	3
Standard error of estimate Sy:	0,078
Standard error of procedure Sx:	2,513

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Limit of detection: 4,180µg/L
Limit of quantification: 15,352µg/L

Note: The result depends on the chosen injection volume and the purity of used gases, reagents and ultra-pure water.

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Application News

No. SCA-130-519

Sum parameter – Total Organic Carbon

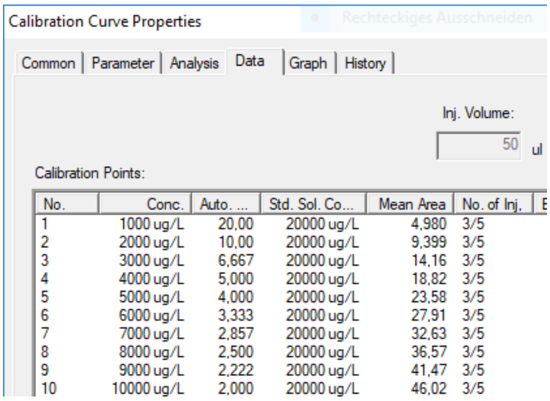
Determination of limit of detection and quantification for the NPOC method (10mg/l range) using the High Salt Catalyst

■ Measurement parameters

System:	TOC-L CPH or CPN
Catalyst:	High Salt Catalyst (Pt-coated balls of various size)
Method:	NPOC (IC-removal)
Acidification:	1,5%
Sparge time:	1,5 min
Injection vol.:	50µl

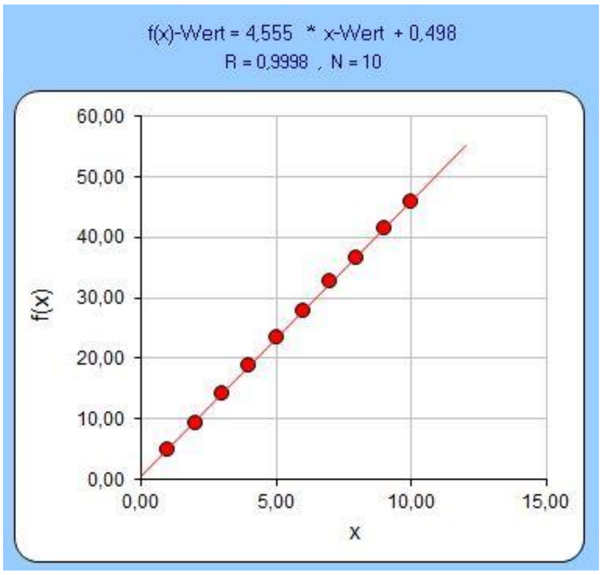
■ Calibration with automatic dilution function

A 10-point calibration curve is carried out by using the automatic dilution of a 20mg/L C stock solution.



No.	Conc.	Auto. ...	Std. Sol. Co...	Mean Area	No. of Inj.
1	1000 ug/L	20,00	20000 ug/L	4,980	3/5
2	2000 ug/L	10,00	20000 ug/L	9,399	3/5
3	3000 ug/L	6,667	20000 ug/L	14,16	3/5
4	4000 ug/L	5,000	20000 ug/L	18,82	3/5
5	5000 ug/L	4,000	20000 ug/L	23,58	3/5
6	6000 ug/L	3,333	20000 ug/L	27,91	3/5
7	7000 ug/L	2,857	20000 ug/L	32,63	3/5
8	8000 ug/L	2,500	20000 ug/L	36,57	3/5
9	9000 ug/L	2,222	20000 ug/L	41,47	3/5
10	10000 ug/L	2,000	20000 ug/L	46,02	3/5

■ Calculation of limit of detection and quantification according to DIN 32645



Characteristics

Slope a:	4,555
Intercept b:	0,498
Correlation coefficient r:	0,9998
Result uncertainty:	33,3%
Probability of error (a):	5,00%
Number of injections:	3
Standard error of estimate Sy:	0,211
Standard error of procedure Sx:	0,046

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Limit of detection:	**0,077mg/L**
Limit of quantification:	**0,281mg/L**

Note: The result depends on the chosen injection volume and the purity of used gases, reagents and ultra-pure water.

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Application News

No. SCA-130-520

Sum parameter – Total Organic Carbon

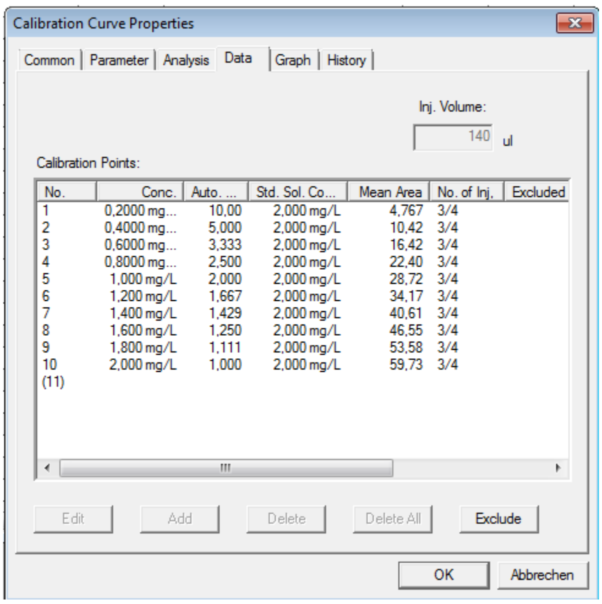
Detection and determination limit of TN method with TOC-L CXN

■ Measurement parameters

System:	TOC-L CPN
Catalyst:	Standard catalyst (Al-balls covered with Pt)
Method:	TN (with TNM-L)
Injection vol.:	140µl

■ Calibration with automatic dilution function

A 10 point calibration curve is carried out by using the automatic dilution of a 2mg/L TN (based on NO_3) stock solution.


Calibration Curve Properties

Common | Parameter | Analysis | Data | Graph | History

Inj. Volume: 140 ul

Calibration Points:

No.	Conc.	Auto. ...	Std. Sol. Co...	Mean Area	No. of Inj.	Excluded
1	0,2000 mg...	10,00	2,000 mg/L	4,767	3/4	
2	0,4000 mg...	5,000	2,000 mg/L	10,42	3/4	
3	0,6000 mg...	3,333	2,000 mg/L	16,42	3/4	
4	0,8000 mg...	2,500	2,000 mg/L	22,40	3/4	
5	1,000 mg/L	2,000	2,000 mg/L	28,72	3/4	
6	1,200 mg/L	1,667	2,000 mg/L	34,17	3/4	
7	1,400 mg/L	1,429	2,000 mg/L	40,61	3/4	
8	1,600 mg/L	1,250	2,000 mg/L	46,55	3/4	
9	1,800 mg/L	1,111	2,000 mg/L	53,58	3/4	
10	2,000 mg/L	1,000	2,000 mg/L	59,73	3/4	
(11)						

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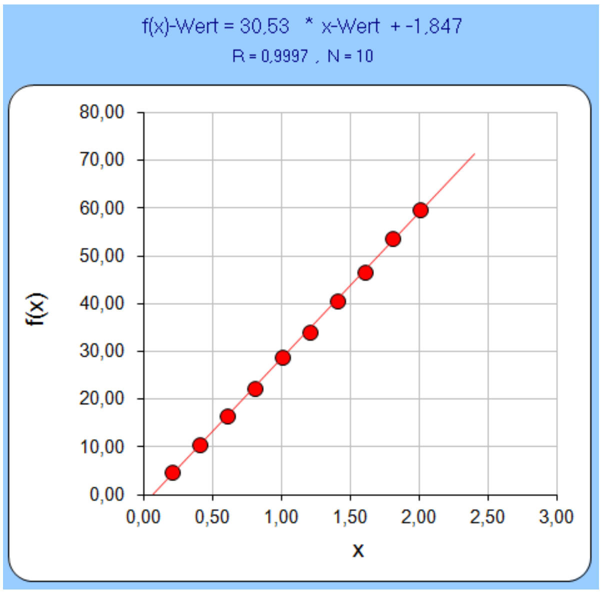
■ Calculation of detection and determination limit according to DIN 32645 (based on linear regression)



Characteristics

Slope a:	30,531
Intercept b:	-1,847
Correlation coefficient r:	0,9998
Result uncertainty:	33,3%
Probability of error (a):	5,00%
Number of measurements n:	3
Standard error of estimate Sy:	0,426
Standard error of procedure Sx:	0,014
Sum of squared deviations:	3,3
Quantile (one-sided):	1,860
Quantile (two-sided):	2,306

Limit of detection: 0,023mg/L
Limit of quantification: 0,084mg/L

Note: The results depend on the selected injection volume, the purity of the vessels, water, chemicals and gases used.

6. TOC process analysis

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

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

The TOC-4200 stands out not only in terms of its robustness but also by its reliability. The TOC-4200 already integrates the most advanced communication channels to the control room. In addition to the conventional communication modes, a Modbus communication protocol is available. An optional web browser enables access to the instrument from any network-connected computer.

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

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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_2 using a catalyst under high temperatures with subsequent detection of the resulting CO_2 using an NDIR detector
- wet chemical oxidation, which applies a combination of UV irradiation and persulfate for oxidation. The resulting CO_2 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.

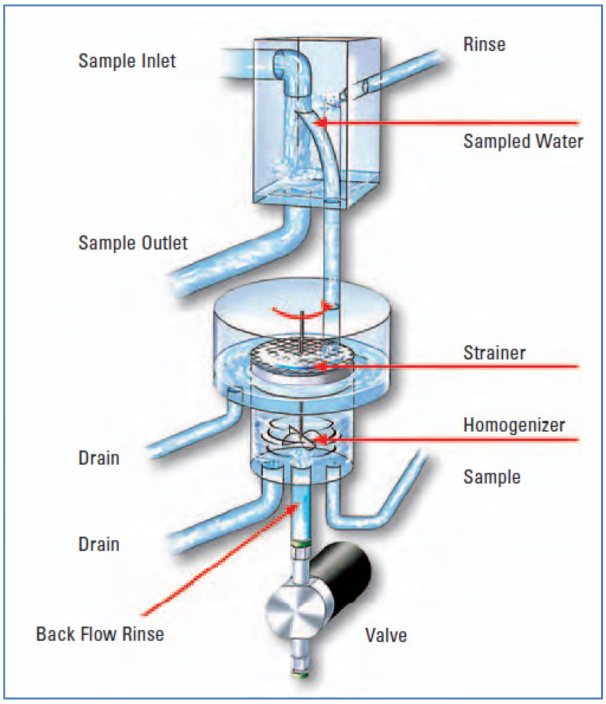

Fig. Multi-Stream switcher

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 chose the measuring sequence of the sample streams.

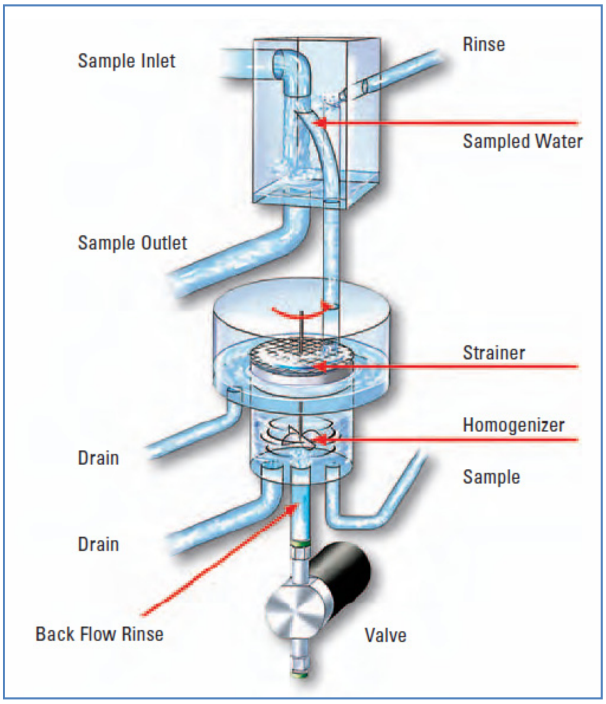

Fig.: Multi-stream suspended solids pretreatment unit

■ Recommended analyzer / Configuration

TOC-4200

Multi-stream suspended solid pretreatment unit

Acid rinse system

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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_2. The highly sensitive NDIR detector allows small injection volumes (typically 20 - 50 µL) that reduce the absolute sample input onto the catalyst. A further reduction can be achieved using the integrated dilution function.

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

■ Kit for high-salt samples

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

■ TOC-4200 in daily practice

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

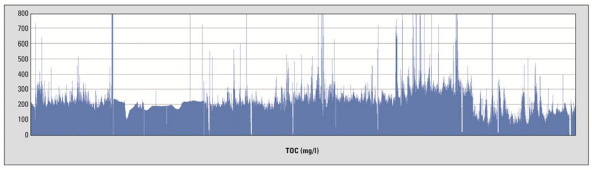

Fig. Diagram of 27.000 Measurement results (three months)

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

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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_2 using a catalyst under high temperatures with subsequent detection of the resulting CO_2 using an NDIR detector
- Wet chemical oxidation, which uses a combination of UV irradiation and persulfate for oxidation. The resulting CO_2 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.

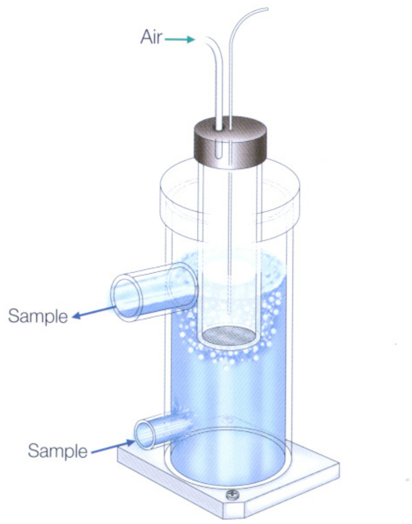


Fig. Sampling

■ TOC measuring method

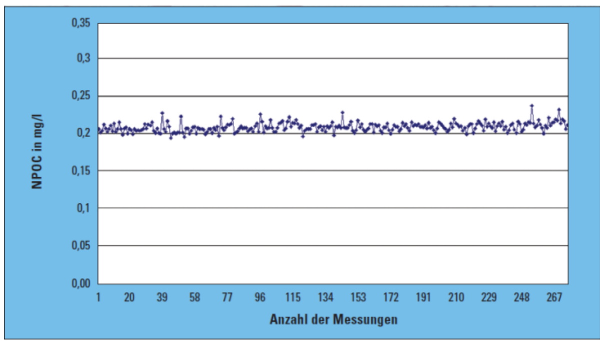
TOC determination is often carried out via the NPOC method, whereby the inorganic carbon content (carbonates and hydrogen carbonates) is removed prior to the actual analysis. For this purpose, the sample is drawn from the continuous sample stream into a syringe and automatically acidified via the 8-port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

Using the sparging gas connection, the CO_2 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

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Shimadzu Europa GmbH
www.shimadzu.eu

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Application News

Sum parameter – Total Organic Carbon

TOC-4200 - High Sensitivity Measurement Option

No. SCA-130-605

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

■ TOC (Total Organic Carbon)

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

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

■ TOC-4200

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

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

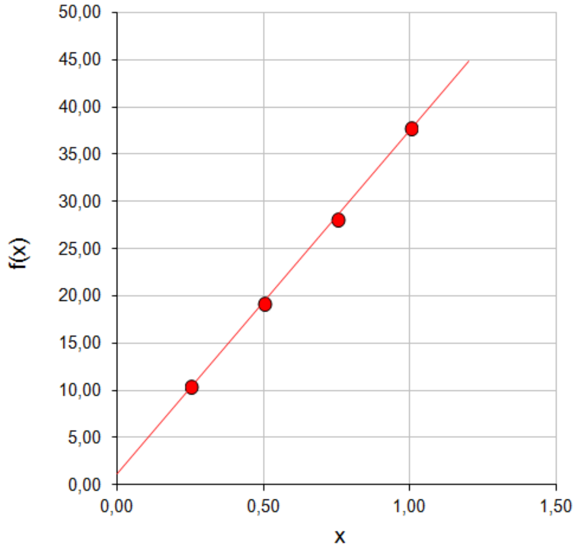
Numerous status and alarm signals simplify detection of exceeded limit levels and indicate the need for maintenance. A Modbus communication channel complements the conventional communication modes. An optional web browser gives access to the instrument from any networked computer.

■ High Sensitivity Measurement Option

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

■ Calibration Curve

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



■ Calibration Curve Characteristics

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

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

Analytical limits according to DIN 32645

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

■ Recommended analyzer / Configuration

TOC-4200
High Sensitivity Measurement Option
Carrier Gas: High-purity air or High-purity nitrogen, (N_2 Carrier Gas High Sensitivity Measurement Option required)

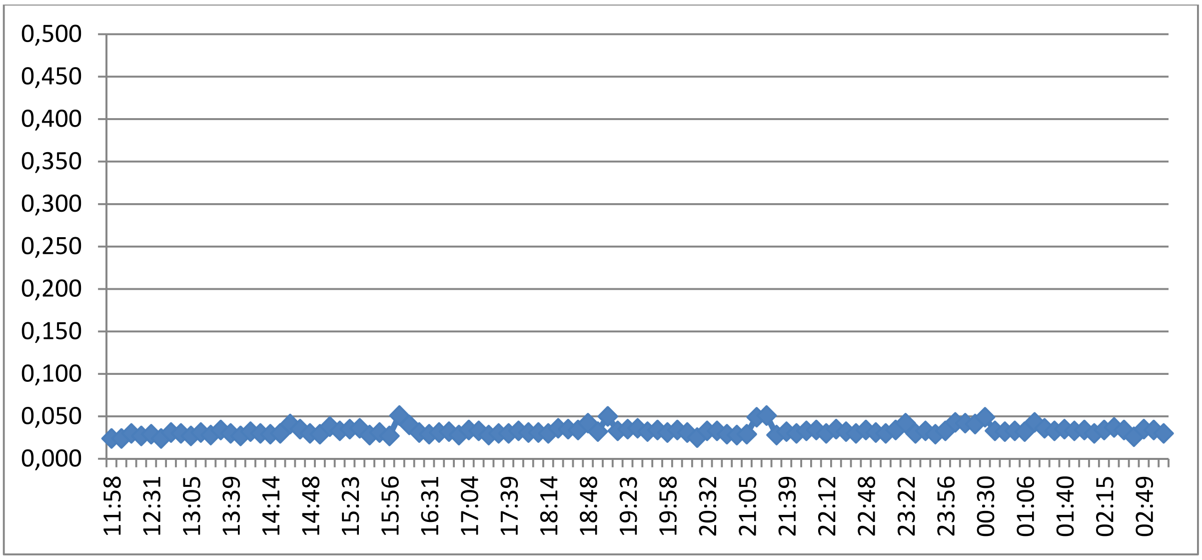


Fig. TOC-4200 Measurement results in mg/l of ultra pure water

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Application News

No. SCA-130-606

Sum parameter – Total Organic Carbon

Continuous TOC determination on airports

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

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

■ Continuous online NPOC monitoring

Important for TOC determination is the differentiation between organic and inorganic carbon. Carbonates and hydrogen carbonates are, after all, present in all natural waters. The most widely used method for TOC determination is the so-called NPOC method. In this method, the sample is acidified to convert the carbonates and hydrogen carbonates present in the sample to CO_2. The resulting carbon dioxide is subsequently purged using a gas stream passed through the sample.
TOC (Total Organic Carbon) is a measure of the concentration of organically bound carbon and therefore reflects the pollution level of organic substances in wastewater.
Depending on the use of the de-icing agent, the TOC values can fluctuate significantly.

■ Tried and tested and powerful – the TOC-4200

The TOC-4200 process analyzer is perfectly designed for this application. The TOC-4200 is a powerful analyser that uses catalytic combustion at 680 °C. After the analyser has automatically removed the inorganic carbon, a sub-quantity is injected onto a hot (680 °C) platinum catalyst. Here, all organic components present are oxidized to carbon dioxide. The resulting CO_2 is transported by a carrier gas stream to a highly sensitive and CO_2 selective NDIR detector, where it is measured. The TOC concentration is calculated using an external calibration.

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

■ Multiple sample streams in one instrument

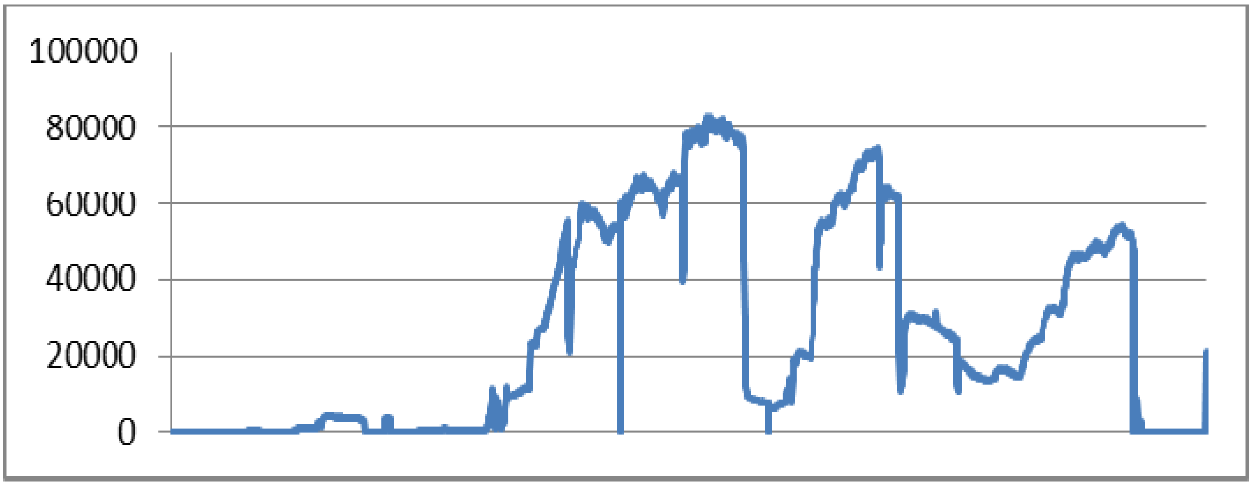
An airport may have several separate wastewater collection systems. In this case, multiple sample streams must be measured using one instrument, requiring the use of a multi-stream sampler. The sample is passed through a strainer and reaches the sample chamber where it is homogenised using a rotating knife before being transferred to the instrument for further analysis. In this way, even samples containing large amounts of particulate matter can be measured without any problems. After sampling, the chamber and strainer are cleaned with rinsing water. The rinsing water prevents carry-over effects when switching sample streams. The measuring parameter can be selected individually for each sample stream. In addition, the user can freely select the sequence by which the sample streams are to be measured.

■ Conclusion

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

■ Recommended Analyser / Configuration

TOC-4200
Stand set
Multi-stream unit (for suspended samples)



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

Application News

No. SCA-130-608

Sum parameter – Total Organic Carbon

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

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

■ ISP-Module in TOC-4200

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

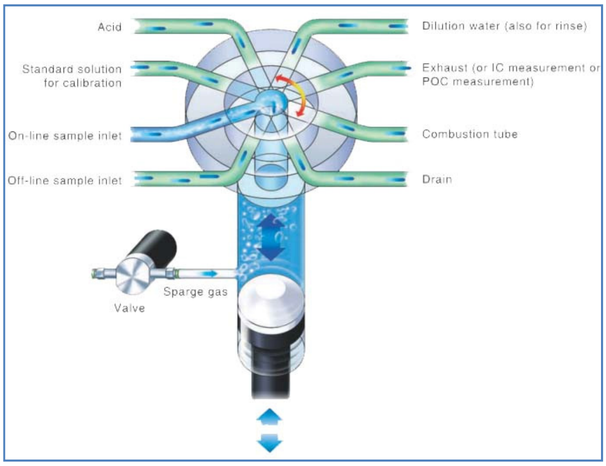


Figure: ISP-module in TOC-4200

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

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

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

Calibration

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

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

Glucose standard

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

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

■ TOC-Determination of a high concentrated Glycol solution

TOC-determination on airports is one of the applications where the TOC values can fluctuate significantly depending on the use of the de-icing agent. The de-icing agent that is most frequently used is a mixture of water, glycol and additives.
Due to this, the test is repeated with a glycol solution in different concentration.

1. Glycol Solution

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

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

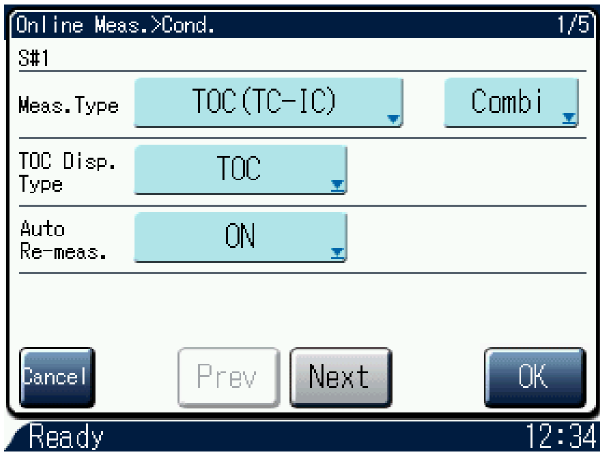
2. Glycol Solution

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

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

■ Function “Auto Re-measurement“

The previous measurements are done with a fixed dilution factor of 40. But which parameter should be set if the samples with high concentration are exceptional cases only?
In this case, the TOC-4200 provides the function “Auto RE-measurement”.



This function allows setting of the parameters for the normal measurement (lower measurement range, un-diluted or low dilution factor).
If the measurement value exceeds the calibrated range, the injection volume and dilution factor are automatically updated and measurement is performed again.

■ Conclusion

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

■ Recommended Analyzer / Configuration

TOC-4200

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Application News

No. SCA-130-609

Sum Parameter – Total Organic Carbon

TOC-4200 – Carryover free TOC determination

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

■ Example: wastewater treatment plant

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

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

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

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

■ ISP-Module in the TOC-4200

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

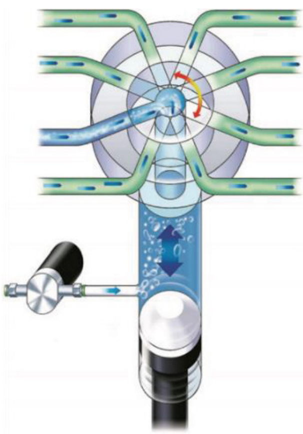


Fig.: ISP-Module TOC-4200 Series

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

■ Sampling method

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

■ Practical test

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

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

■ Conclusions

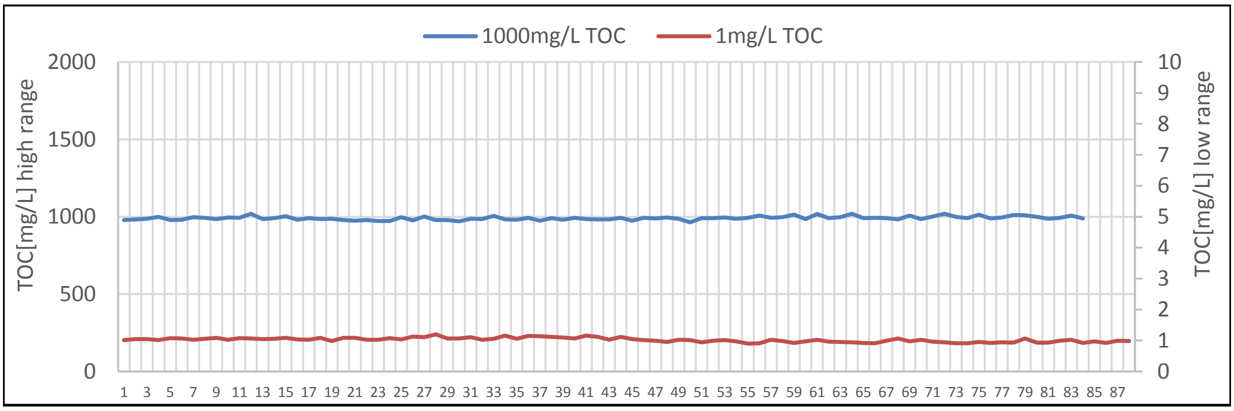
	S#1	S#2
Mean Value TOC (mg/l)	1,02	992,67
Standard deviation (mg/l)	0,07	13,32

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

■ Recommended analyzer / Configuration

TOC-4200

Individual sampling system



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Application News

No. SCA-130-610

Sum Parameter – Total Organic Carbon

Monitoring of cooling water with TOC-4200

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

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

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

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

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

■ TOC determination in cooling water

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

- Catalytic combustion, where carbon compounds are converted into CO_2 using a catalyst under high temperatures with subsequent detection of the resulting CO_2 using an NDIR detector
- Wet chemical oxidation, which uses a combination of UV irradiation and persulfate for oxidation. The resulting CO_2 is either detected via an NDIR detector or via conductivity detector.

When applying TOC determination to cooling water, usually few particles are expected, but here as well, it is better to be on the safe side with the higher oxidation potential offered by catalytic combustion. It is important to be able to quickly and reliably detect every possible organic contamination. The analyser availability is maximized by a combustion at temperatures below the melting points of common salts.

■ TOC-4200

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

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

■ Sampling technique

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

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

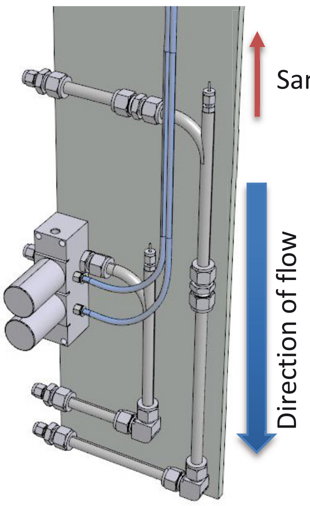


Fig.: Counter-flow sampler for 3 streams

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

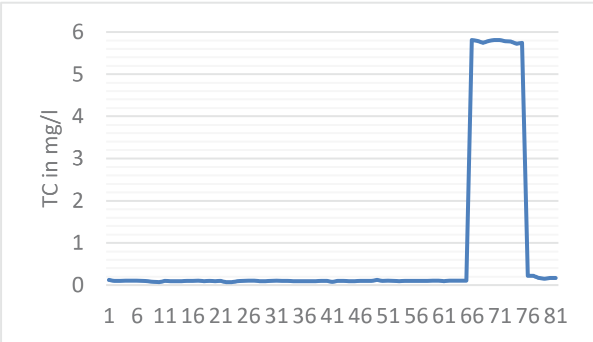
The number of sample streams the TOC-4200 monitors, can be optionally extended to a maximum of six.

■ Measurement method

The TC method is often used for the monitoring of cooling water. In this case the sum of organic (TOC including POC) and inorganic (TIC) carbon compounds is determined.
For this purpose, the sample is drawn with a syringe pump from the continuous sample stream and then injected into the oxidation unit using a septum-free slider mechanism. Using TC analysis with its low cycle times of 2-3 minutes allows for a very fast process adjustment. The dilution function of the syringe pump enables dynamic expansion of the measurement range so that exact values are obtained even if a heat exchanger ruptures. No additional detectors are necessary for this.

■ TC response behavior

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



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

■ Recommended analyser / Configuration

TOC-4200
Counter-flow type sampling mechanism

Application News

No. SCA-130-611

Sum Parameter – Total Organic Carbon

Continuous TOC determination in Petrochemistry

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

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

■ Requirements to modern refineries

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

■ Environmental protection

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

■ TOC-4200

The high-performance TOC-4200 analyser applies catalytic combustion at 680 °C. The powerful oxidation allows complete and rapid detection of both dissolved and undissolved compounds, and enables the direct detection of all contained hydrocarbons. Depending on the sample characteristics, the total inorganic carbon (TIC) and the volatile organic carbon (POC) can be measured in addition to TOC and TC. In order to measure the total bound nitrogen (TN), the TOC-4200 can be upgraded with a specific module.
The consistent usage of inert materials reduces the risk of cross-contamination through the absorption and desorption of oils and fats. All fluid paths, including the sample supply line, are additionally purged and rinsed between each measurement.

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

■ Sampling technique

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

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

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

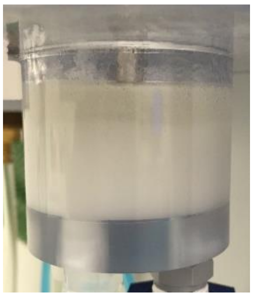


Fig.: Mechanically created emulsion

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

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

■ Installation site

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

Fig.: TOC analyser in pressurized cabinet

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

■ Recommended analyser / configuration

TOC-4200

Individual sampling system

Optional enclosure for zone 1 or 2

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