



1. Environmental analysis

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

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

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

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

The relevance of the TOC parameter becomes clear when looking at the parameter lists of various regulations in European countries: the Waste Disposal Ordinance, the Waste Technical Guidelines, the Landfill Ordinance, the Ordinance pertaining to the Recovery of Waste, the 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.'

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 regrowth 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 ($\text{TOC} = \text{TC} - \text{IC}$) 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%) \pm 2 mg/l
(98 – 102 mg/l)

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

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

TOC (calc.) = 2 mg/l \pm 3,96 mg/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.

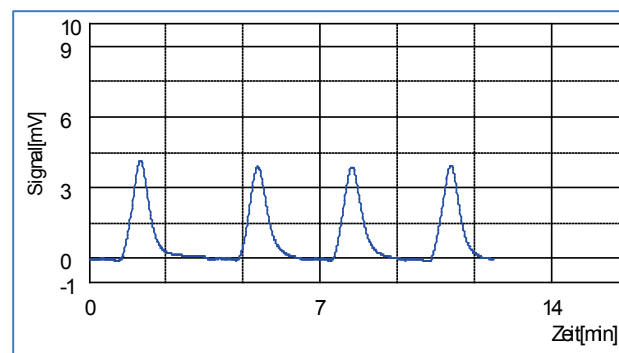
The ISP (integrated sample preparation) module consists of an 8-port valve and a syringe with sparging gas connection. In addition to acidification and sparging in the syringe, the ISP also enables automatic dilution. This feature facilitates an extended measuring range, dilution of highly contaminated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

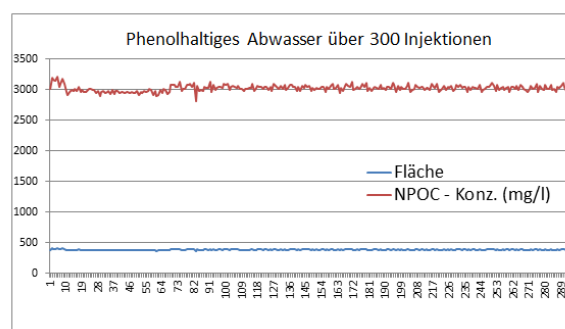
- 1) water whose properties have been changed by domestic, commercial, agricultural or other use and the water (sewage) discharged with it during dry weather conditions as well as
- 2) the run-off and collected water (rainwater) from built-up or paved areas following precipitation.

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 inhomogeneity of the particles by sedimentation within the syringe body, multiple injections from the same syringe may not be carried out in this case.



■ Recommended Analyzer / Configuration

TOC-L_{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)

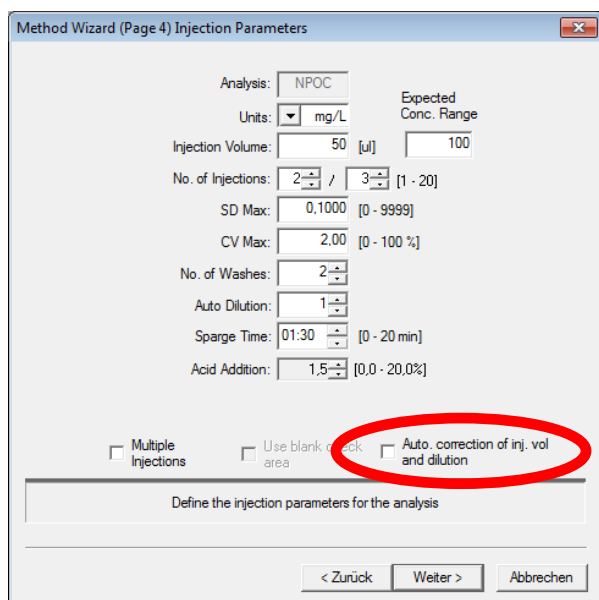
Depending on the region, high TIC concentration (> 100 mg/L) can also occur in surface water as well as in groundwater.

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

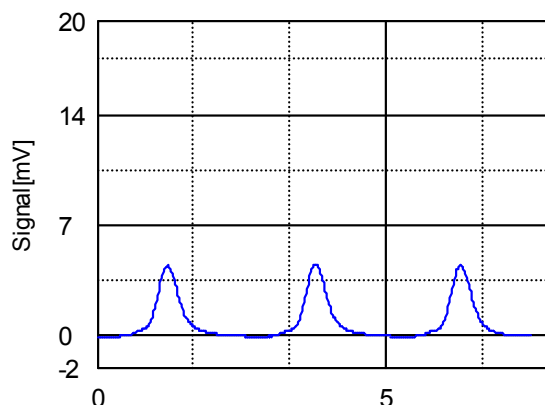
■ TOC-L

To prepare the sample accordingly, the ISP module of the TOC-L automatically acidifies the sample and strips the CO₂ originating from the TIC.

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



■ Example: River water



NPOC-Method

Acidification: 1,5%

Spurge-time: 5 Minutes

TOC-Concentration: 3,4 mg/l

RSD (3 Injections): 1,4%



■ Recommended analyzer / Configuration

- TOC-L_{CPH}

- ASI-L (40ml) with stirrer option

- External Spurge-Kit

(1) Source: Wikipedia

Application News

No. SCA-130-104

Sum parameter – Total Organic Carbon

TOC – Determination in seawater

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



■ Seawater samples

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

■ Are high salt loads a problem?

During thermal catalytic combustion of the test sample, the dissolved salts crystallize. Depending on the salt concentration, this can affect or clog the system. Maintenance measures (for instance exchanging the catalyst) would then be required in order to render the instrument operational again. Of course, it is desirable to keep the maintenance intervals as long as possible.

■ TOC-L Series

The TOC-L series offers various possibilities to keep the maintenance need for highly polluted samples as low as possible. The analyzers are operated under catalytic combustion at 680 °C. This temperature is lower than the melting point of sodium chloride and therefore prevents deactivation of the active centers of the catalyst by a melt. The use of the platinum catalyst ensures complete conversion of organic carbon compounds to CO₂.

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

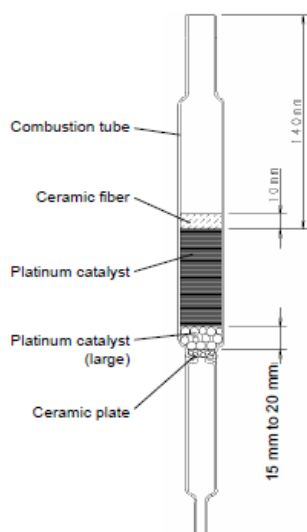


■ Kit for high-salt samples

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 NaSO₄ 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 ₂ SO ₄	888°C
MgCl ₂	708°C
CaCl ₂	782°C
K ₂ SO 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.

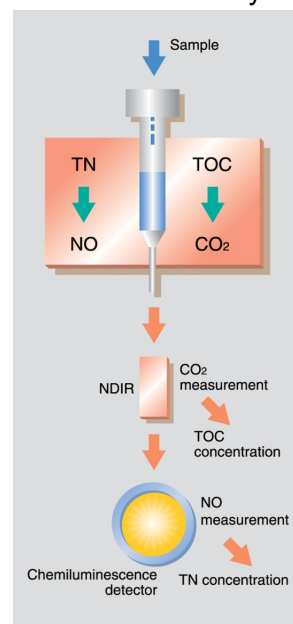


Figure: Simultaneous TOC/TN-Determination

■ Recommended analyzer / Configuration

TOC-L_{CPN}

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

Kit for high-salt samples

TNM-L

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, AbfAbIV), TOC in solid materials is one of the key parameters for the characterization of wastes as part of the acceptance control of landfills. This important control measure requires a fast and simple TOC determination method and, at the same time, a robust and statistically reliable method that is based on the inhomogeneous composition of soils.



To date, the established regulations describe a method whereby a weighed solid sample is combusted in a stream of air or oxygen. The CO₂ 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



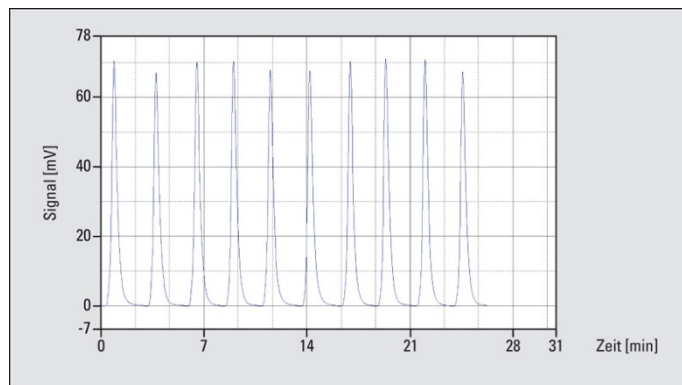
Approximately 200 mg of the dried and ground sample is weighed into an Erlenmeyer flask. The sample is subsequently suspended in a diluted hydrochloric acid solution. The acidic solution serves to break down the carbonates present in the sample and, at the same time, form the suspension medium.

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.

Application News

No.SCA-130-106

Sum parameter – Total Organic Carbon

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

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



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

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

■ Cellulose test according to DIN EN 1484

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

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

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

■ Particle tolerance of the TOC-L series

This test was carried out using a TOC-L system (TOC-L_{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.

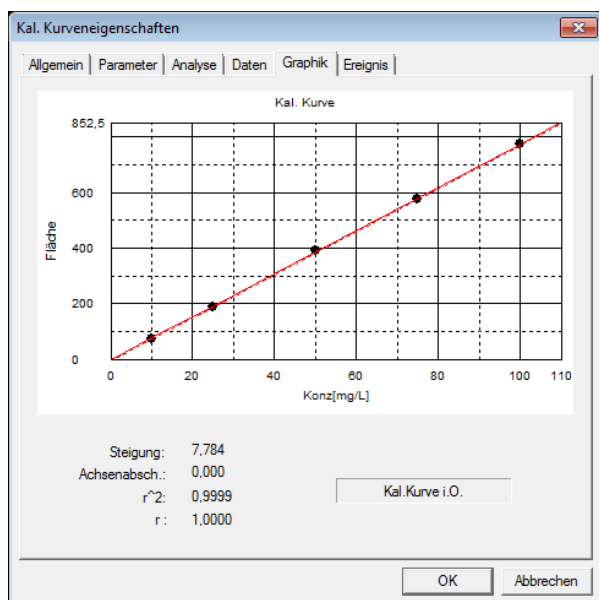


Figure 1 Calibration curve 10-100mg/L

■ 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 = $98,4 \pm 2,2$ mg/l (RSD = 2,27 %).

This corresponds to a recovery of 98,4 %.

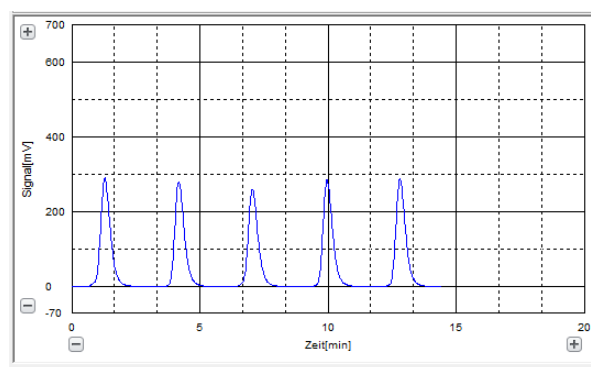


Abb.2 Peak graph of cellulose-suspension

These values are clearly within EN DIN specifications

Application News

No. SCA-130-107

Sum parameter – Total Organic Carbon

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

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



Fig. Used glass fiber filter

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

■ The field test

A TOC analyzer with autosampler was used for the field test. After calibration of the TOC system, the test solution was measured 10 times. The test solution consisted of a glass fiber suspension in hydrochloric acid (five glass fiber filters dispersed in 500 mL) that was continuously stirred during measurement. To test the catalyst, a standard solution with a TOC of 50 mg/L was injected after each 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.

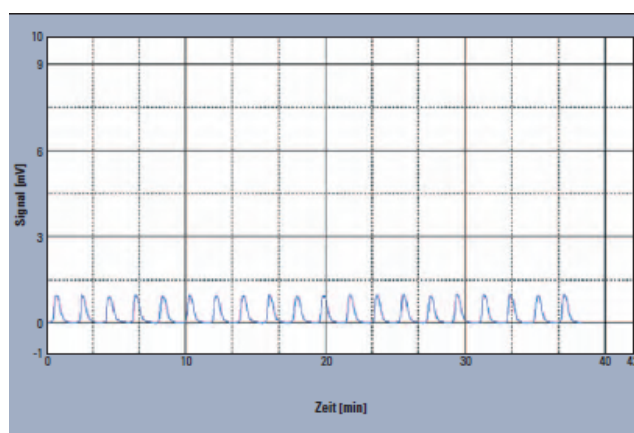


Fig. Peak graphs of the last 20 injections

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
Spurge-Kit.