

5. TOC in daily practice





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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.'

Application News

Sum parameter – Total Organic Carbon

TOC – Determination methods according to EN 1484

No. SCA-130-501

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

■ Definitions according to EN 1484

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

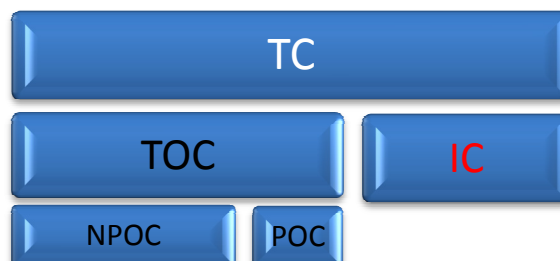
TIC: Total inorganic carbon – the sum of carbon present in water, consisting of elemental carbon, carbon monoxide, carbon dioxide (also carbonates and hydrogen carbonates), cyanide, cyanate, and thiocyanate. TOC instruments mainly detect CO₂, originating from hydrogen carbonates and carbonates, just like TIC.

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

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

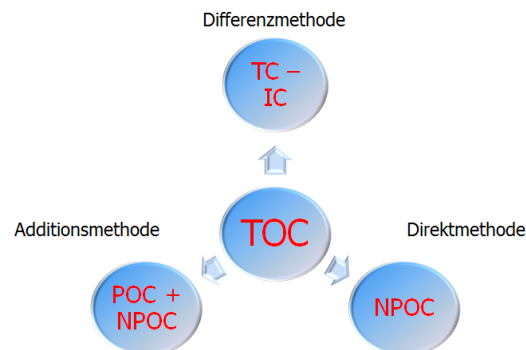
NPOC: Non Purgeable Organic Carbon – the TOC content that is not purgeable under the conditions of this method.

The following graph shows how the parameters are linked:



■ Determination methods

The TOC can be determined according to three different methods:



■ Difference method

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

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

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

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

■ Limitations of the difference method

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

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

Example:

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

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

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

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

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



■ Addition method

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

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

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

The TOC is calculated via addition:

$TOC = POC + NPOC$

■ Direct method

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

NPOC: Acidification of the sample using a mineral acid (for instance HCL) to a pH < 2, whereby carbonates and hydrogen carbonates are completely converted to carbon dioxide. The carbon dioxide is removed from the sample solution via a sparge gas. Direct NPOC measurement (similar to TC measurement) via oxidation to CO₂. 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, CO₂ originating from carbonates and hydrogen carbonates as well as all volatile organic compounds (POC) are purged from the solution. The LiOH trap binds the CO₂ 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 CO₂ 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 CO₂ and transferred to the NDIR detector using a carrier gas.

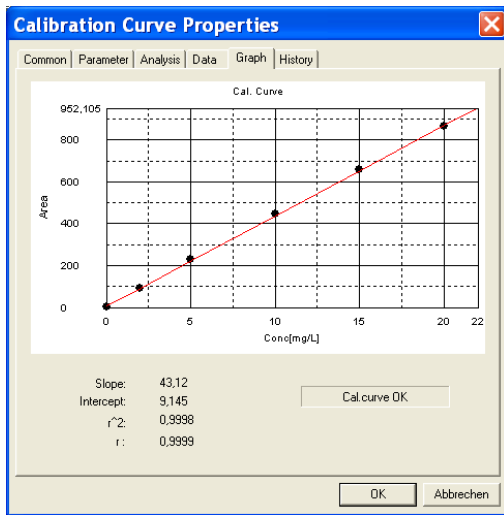


Fig. POC-Calibration with IC-standard

■ System testing

In POC analysis, it is of great importance that the LiOH trap functions perfectly. A test should, therefore, be carried out to confirm the efficiency of the CO₂ trap. This test should be carried out each working day:

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

■ Example of a POC measurement

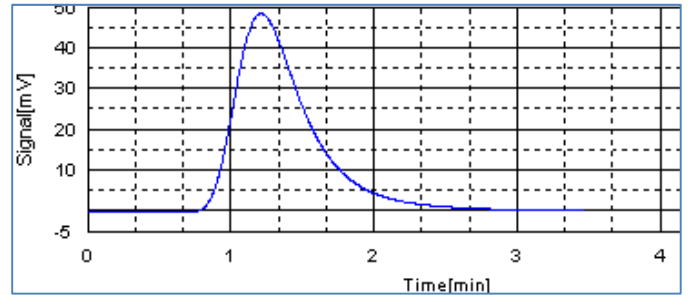
Sample: Toluene in ultrapure water

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

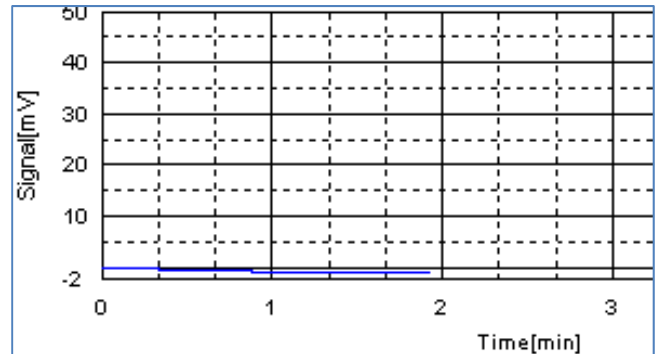
POC measuring method:

Injection volume: 800 µL
Purging time: 3 min

POC-Peak:



NPOC-Peak:



Result:

TOC=4,05mg/l

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

NPOC=0mg/l

■ Recommended Analyzer / Configuration

TOC-L_{CXX}
ASI-L
POC-Option

Application News

Sum parameter – Total Organic Carbon

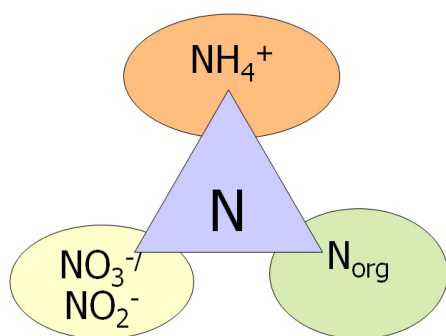
TN_b – total bound nitrogen

No. SCA-130-503

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

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

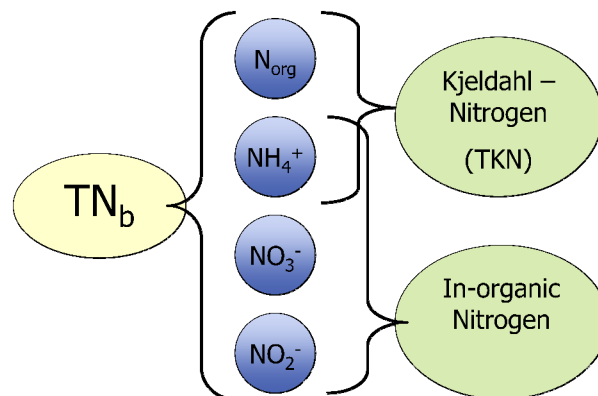
Bound nitrogen occurs in nearly all waters, mostly in the form of ammonia, nitrate, nitrite or organic compounds.



■ Total nitrogen TN_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 (NO₂*). In the subsequent reaction to NO₂, 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 CO₂ 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).

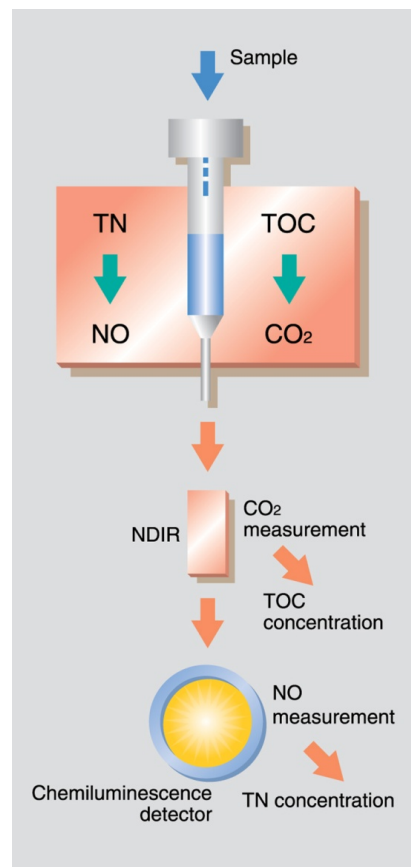


Fig. Simultaneous TOC/TN-Determination

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

Application News

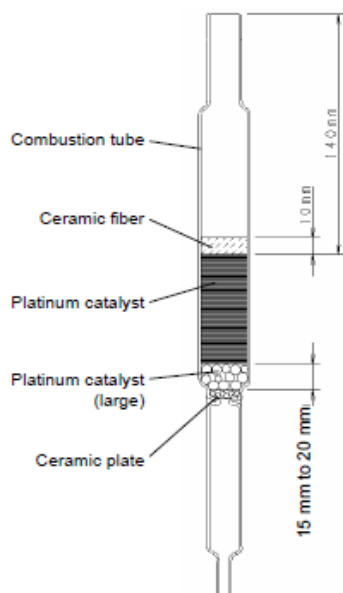
Sum parameter – Total Organic Carbon

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 CO₂ 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 Na₂SO₄ 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

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.

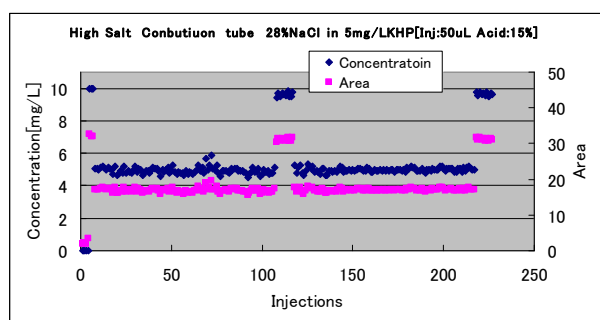


Fig. Results of endurance test

■ 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.)

Application News

No. SCA-130-505

Sum parameter – Total Organic Carbon

Kit for small sample volumes

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



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

■ Small sample volumes

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

■ Specification

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

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

TN: to 200 mg/L

Injection volume: 150µl maximal

Diameter: 0.2 mm

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

ASI-L: 9ml Rack

■ Example

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

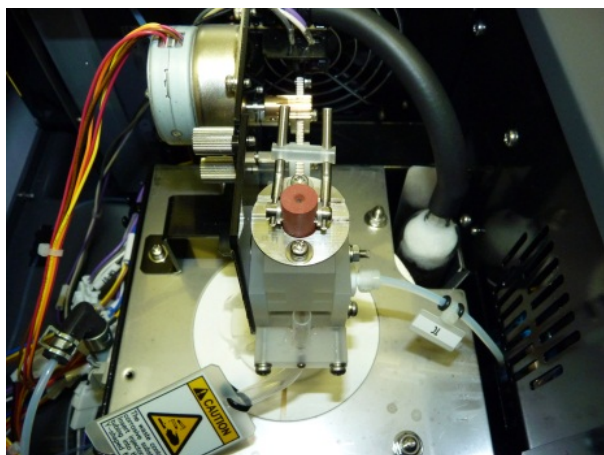
Application News

Sum parameter – Total Organic Carbon

Kit for manual injection

No. SCA-130-506

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.

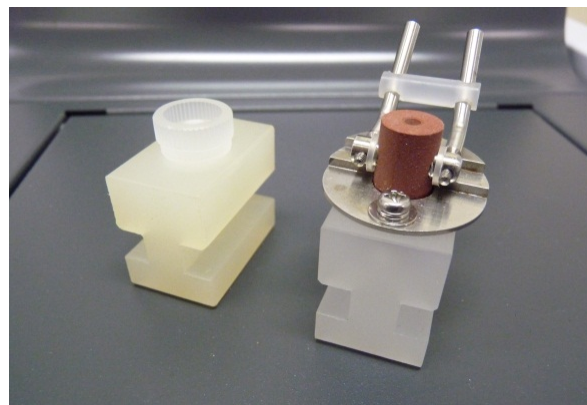


The kit for small sample volumes is a module for TOC analyzers that can be used for automated sample preparation and analysis of small sample amounts. The methods can be optimized in such a way that only a few mL of the sample are required. Optimization should, however, not be at the expense of the intermediate 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: 150 μL 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: 20 μL bis 10mL
Measurement time: 2 – 4 Minuten
Reproducibility: RSD: 2%

Application News

No. SCA-130-507

Sum parameter – Total Organic Carbon

Calibration with automatic dilution function



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

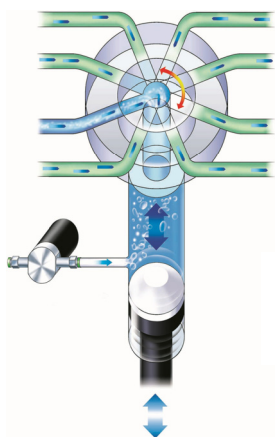
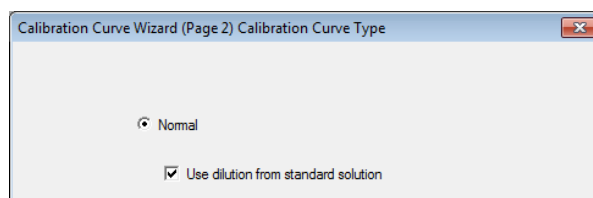


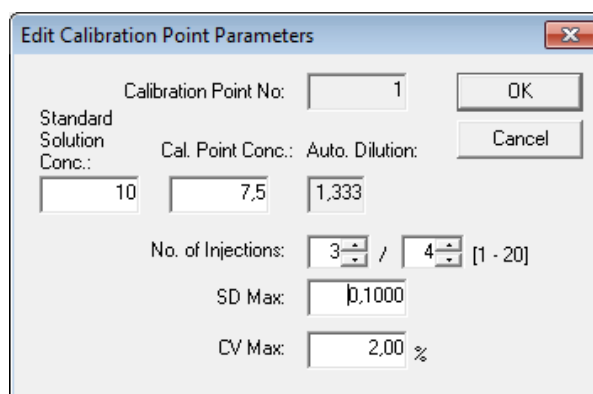
Fig. ISP-Module of TOC-L series

■ Calibration with automatic dilution function

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



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

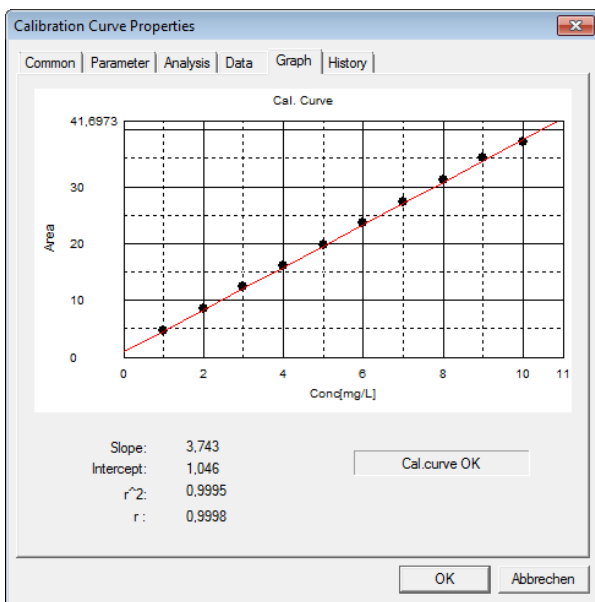


Since fractional factors are allowed, it is possible to create a 10-point calibration curve with equidistant concentration intervals from one standard solution.

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

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

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

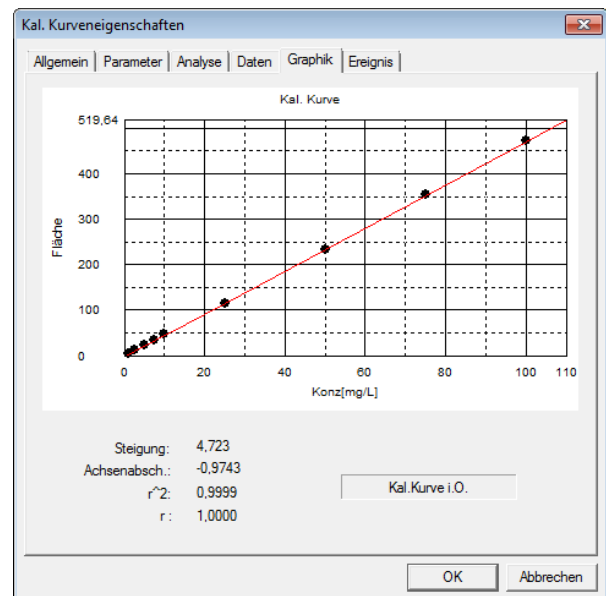


■ Calibration with automatic dilution function over two decades

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

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

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



Application News

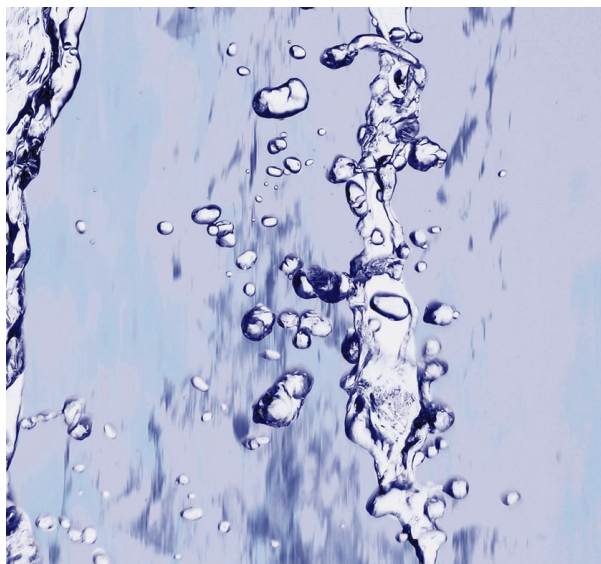
Sum parameter – Total Organic Carbon

Blank value consideration in TOC analysis

No. SCA-130-508

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

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



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

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

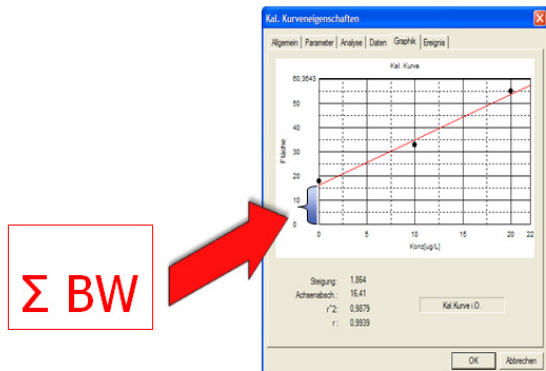
Purified waters that have been produced using highly complex water treatment systems, have different water grades. The DIN ISO 3696 standard specifies the requirements and test methods for water for analytical use and classifies these waters according to 3 grades.

<i>Parameter</i>	<i>Pure water Typ III</i>	<i>Pure water Typ II</i>	<i>Ultra pure water Typ I</i>
Ions, resistance (MΩ.cm)	>0,05	>1,0	>18,0
Ions, resistance (μS/cm)	< 20	<1,0	<0,055
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

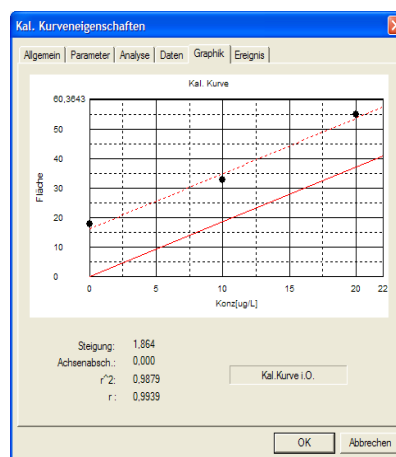
x = TOC – concentration

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.

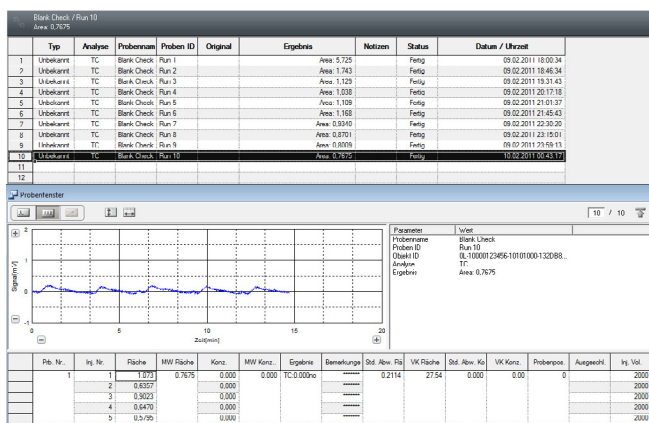
In short: dilution water has a blank value, a sample does not have a blank value.



■ 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) CO₂.



Application News

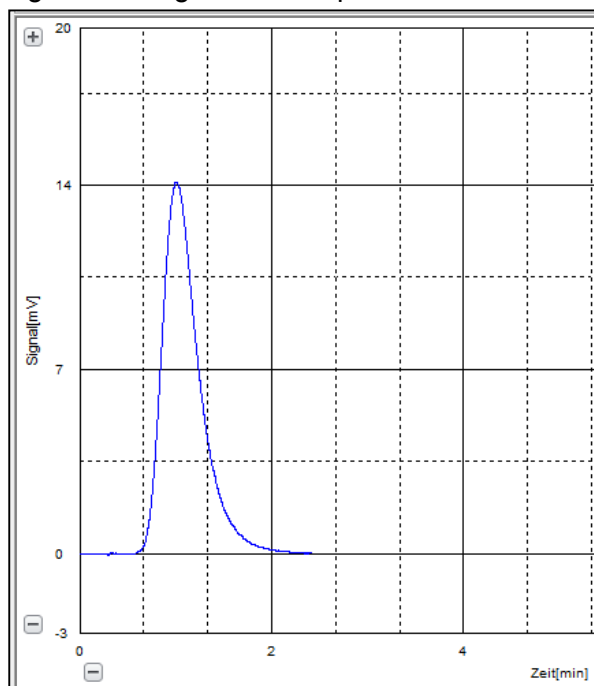
No. SCA-130-509

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 CO₂) is cooled and dehumidified and passed through a halogen scrubber into the cell of the NDIR (Non Dispersive Infrared) detector where the CO₂ 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 CO₂ 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 ₂ SO 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-Phenanthroline	50.0	49.7	99.4
Catechin	50.0	49.1	98.2
1,4-Benzoquinone	100.0	100.4	100.4
Sodium acetate	100.0	98.3	98.3
Nicotinamide	200.0	198.9	99.5
Nicotinamide	100.0	101.3	101.3
Nicotinamide	2.000	1.993	99.7

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

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

Application News

No. SCA-130-510

Sum parameter – Total Organic Carbon

Detection and determination limit of NPOC method with standard catalyst



■ Measurement parameters

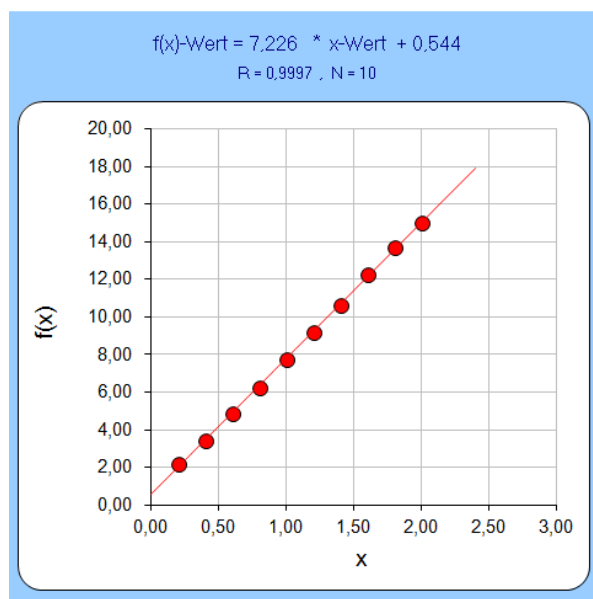
System: TOC-L CPN
 Catalyst: Standard catalyst
 (Al-balls covered with Pt)
 Method: NPOC (removing of IC by acidification and sparging)
 Acidification: 1,5%
 Sparge time: 2 min
 Injection vol.: 150µl

■ 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 µl
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		

■ 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

© DINTEST

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.

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 CO₂ using high temperatures and a catalyst, with subsequent detection of the resulting CO₂ using an NDIR detector.

Wet-chemical oxidation uses a combination of UV irradiation and persulfate oxidation.

■ Wet chemical UV-oxidation

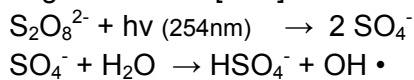
In the wet chemical UV-oxidation, the oxidation power of OH-radicals is used.

T

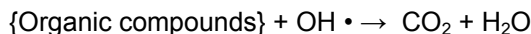
he UV (185nm) activates the H₂O to generate the [OH•] radicals as

$$\text{H}_2\text{O} + h\nu (185\text{nm}) \rightarrow \text{OH}\cdot + \text{H}^+$$

The UV (185nm) also activates the persulfate to generate the [OH•] radicals as



OH radicals are strong oxidants and oxidize the carbon compounds to CO₂.



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

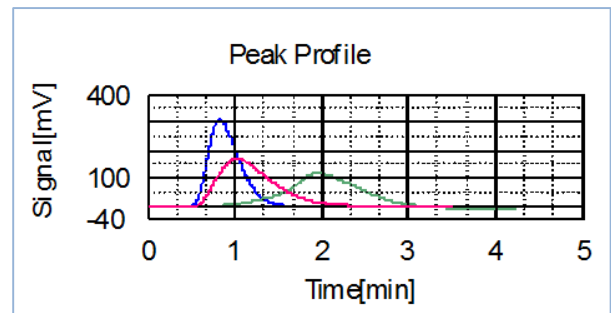


Abb.: Peak graph of KHP standard
(NPOC = 5 mg/l)

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.

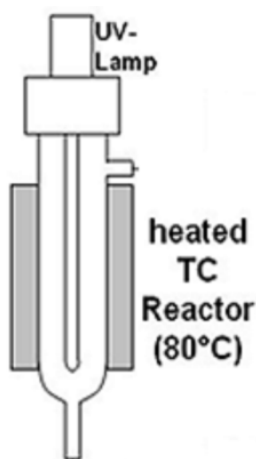


Figure.: TC reactor with integrated UV lamp and heating

■ 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)



Figure: TOC-V_{WP} with ASI-V

■ Recommended analyzer / Configuration

TOC-V_{WP/WS}

ASI-V (with 40ml or 125ml vials)

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 CO₂ 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

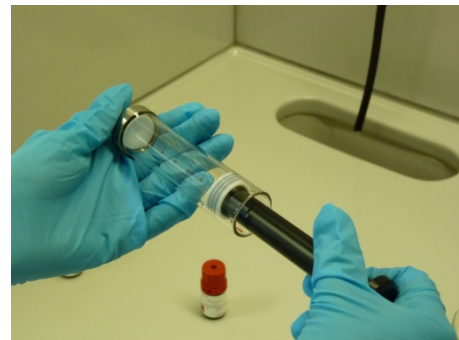
- 1ml N-Methyl-N-(trimethylsilyl)trifluoroacetamide (for GC derivatization, ≥98.5%) – e. g.: von Fluka, No. 69479)
- approx. 20ml methanol
- 1ml syringe with needle

■ 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 drying cabinet)
- 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.

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 be 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

CO₂, 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.

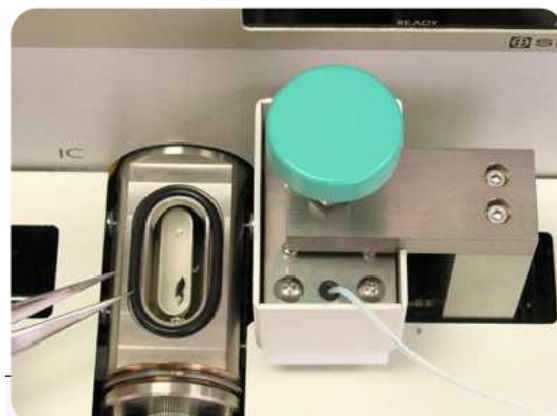
The SSM-5000A solid sample module does not have its own detector, but is coupled to the NDIR detector of the main instrument (TOC-V or TOC-L).

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 CO₂ 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).

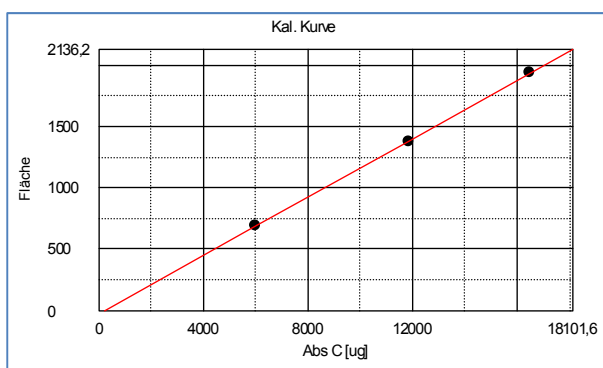


Figure: TC-Calibration with Glucose

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

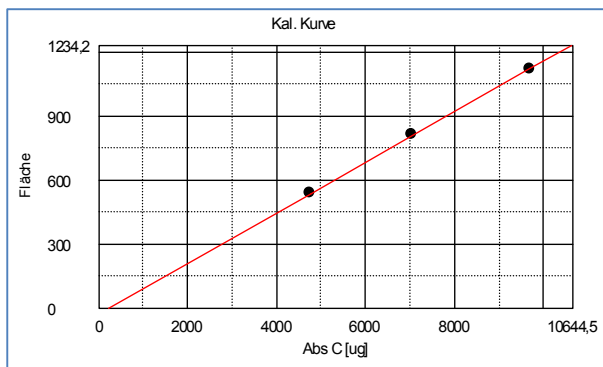
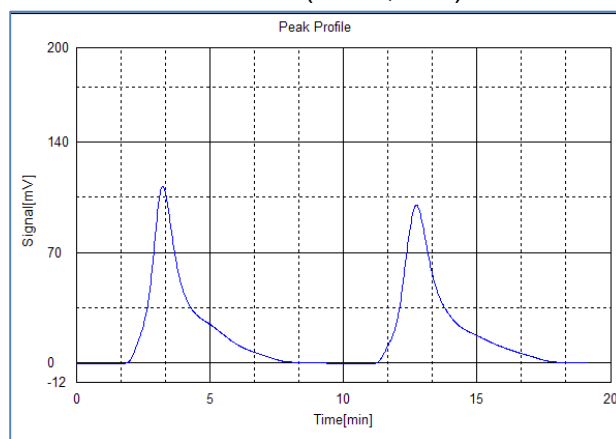


Figure: IC-Calibration with NaHCO₃

■ Example of a real solid sample (Bauxit)

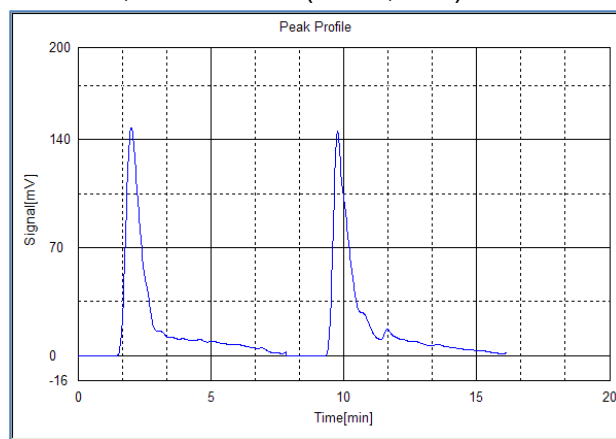
TC determination

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

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 CO₂ is subsequently removed from the sample via sparging with a stream of carrier gas. The remaining organic carbon compounds are then converted to CO₂ via high temperature (catalyst) or wet-chemical oxidation. The amount of CO₂ 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 (C₆H₁₂O₆) 1000mg/L
COD= 1067mg/L
TOC= 400mg/L
Correlation COD/TOC= 2,66

2. Example Acetone (C₃H₆O) 1000mg/L
COD=2207mg/L
TOC= 621mg/L
Correlation COD/TOC= 3,55

3. Example Ethanol (C₂H₆O) 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.

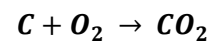
■ COD and TOC in the German Waste Water Ordinance (AbwV)

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 O₂:



As the COD corresponds to the required oxygen amount, the O₂ 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

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

$$\text{for O}_2: 1000 \frac{mg}{L} : 32 \frac{g}{mol} = 31.25 \frac{mmol}{L}$$

The COD factor is derived from the molar ratio of C to O₂:

$$83.33 \frac{mmol}{L} : 31.25 \frac{mmol}{L} = 2.667$$

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

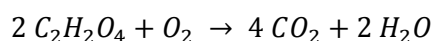
$$COD (O_2) \left[\frac{mg}{L} \right] = TOC \left[\frac{mg}{L} \right] * 2.667$$

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:



4 carbons react with an oxygen molecule.

This is the calculation:

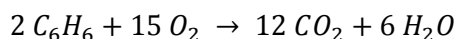
$$\text{for C: } 1000 \frac{mg}{L} : (4 * 12 \frac{g}{mol}) = 20.83 \frac{mmol}{L}$$

$$\text{for O}_2: 1000 \frac{mg}{L} : (1 * 32 \frac{g}{mol}) = 31.25 \frac{mmol}{L}$$

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

■ Benzene

The way oxidation of benzene proceeds:



12 Carbons react with 15 oxygen molecules.

The calculation is as follows:

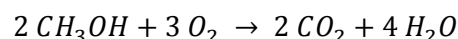
$$\text{for C: } 1000 \frac{mg}{L} : (12 * 12 \frac{g}{mol}) = 6.94 \frac{mmol}{L}$$

$$\text{for O}_2: 1000 \frac{mg}{L} : (15 * 32 \frac{g}{mol}) = 2.08 \frac{mmol}{L}$$

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

■ Methanol

Oxidation of methanol:



2 Carbons react with 3 oxygen molecules.

The calculation is as follows:

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

$$\text{for O}_2: 1000 \frac{mg}{L} : (3 * 32 \frac{g}{mol}) = 10.42 \frac{mmol}{L}$$

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

■ 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).

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.

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.

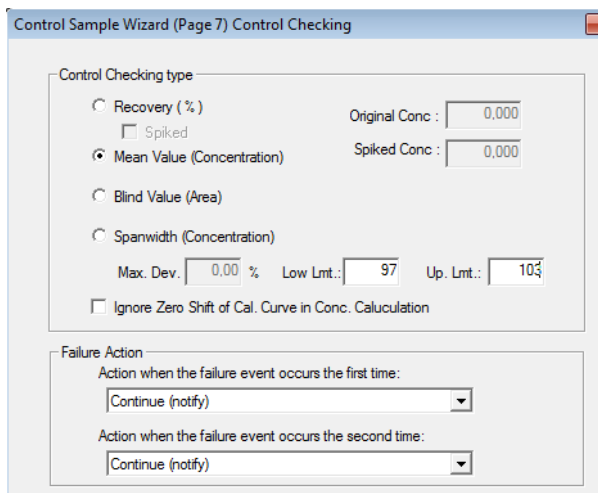


Figure: Control sample parameters.

■ 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.

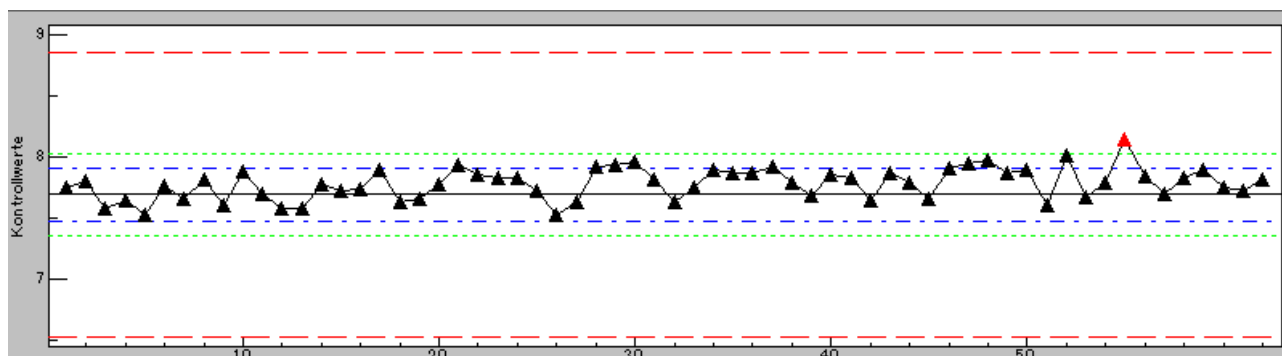


■ Recommended analyzer / Configuration

- 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

Sum Parameter – Total Organic Carbon

Manual injection of low sample volumes

No. SCA-130-517

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 .

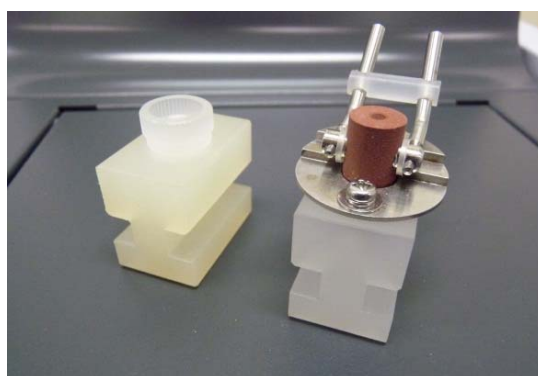


Figure: Injection blocks for manual injection (IC and TC).

■ 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.

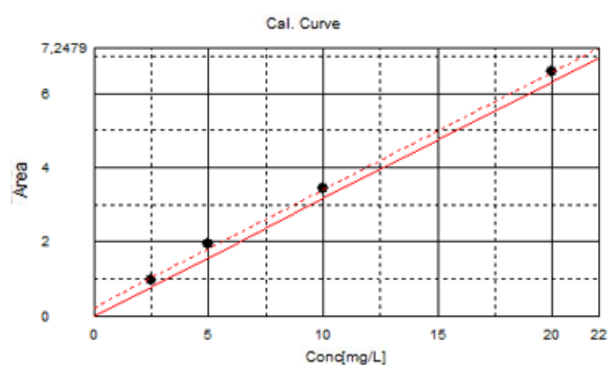


Figure: TC calibration using an injection volume of 5 μL ($r = 0,9996$).

■ 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).

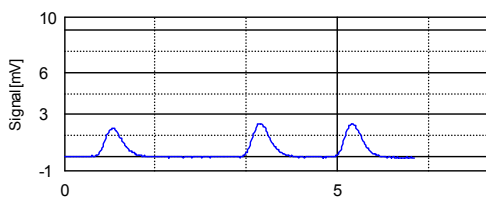


Figure: Peaks of the control sample (15 mg/L)

■ 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.

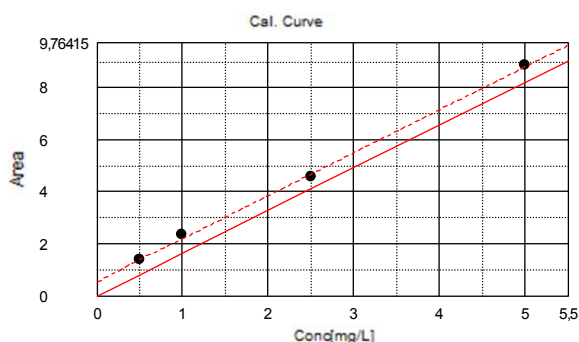


Figure: TC calibration with 20 µL injection volume ($r = 0.9998$).

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

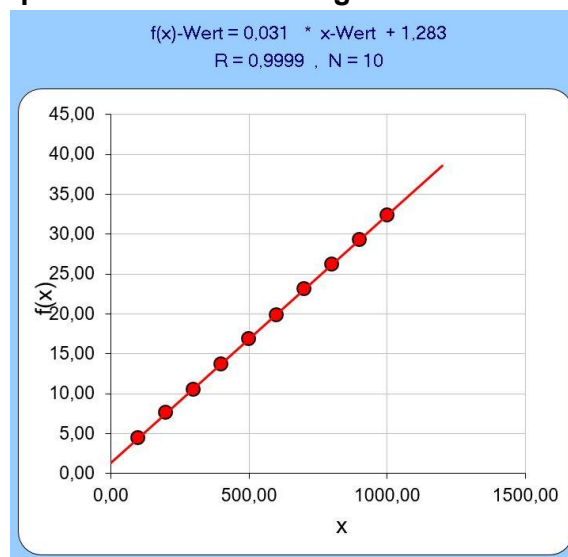
System: TOC-L CPH
Catalyst: High Sensitivity Catalyst (platinum coated wool)
Method: NPOC (IC-removal)
Acidification: 1,5%
Spurge time: 2 min
Injection vol.: 408µl

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 µl
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.

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

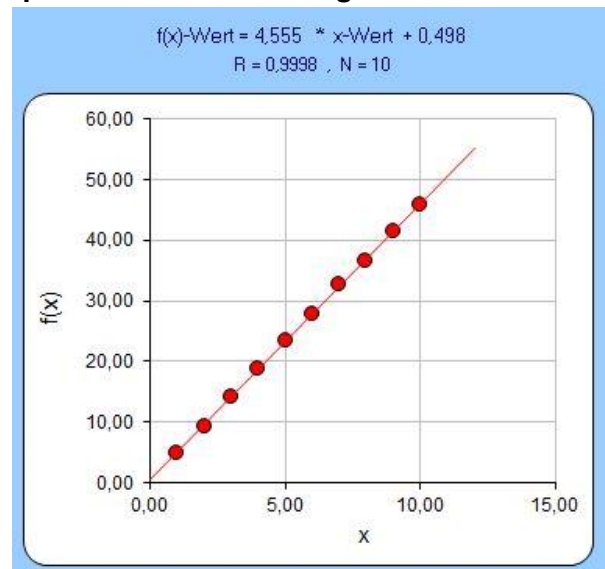
- System: TOC-L CPH or CPN
- Catalyst: High Salt Catalyst
(Pt-coated balls of various size)
- Method: NPOC (IC-removal)
- Acidification: 1,5%
- Sparge time: 1,5 min
- Injection vol.: 50µl

■ 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.

Calibration Curve Properties						
Common Parameter Analysis Data Graph History						
						Inj. Volume: 50 µl
Calibration Points:						
No.	Conc.	Auto. ...	Std. Sol. Co...	Mean Area	No. of Inj.	E
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.

Application News

No. SCA-130-520

Sum parameter – Total Organic Carbon

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



■ Measurement parameters

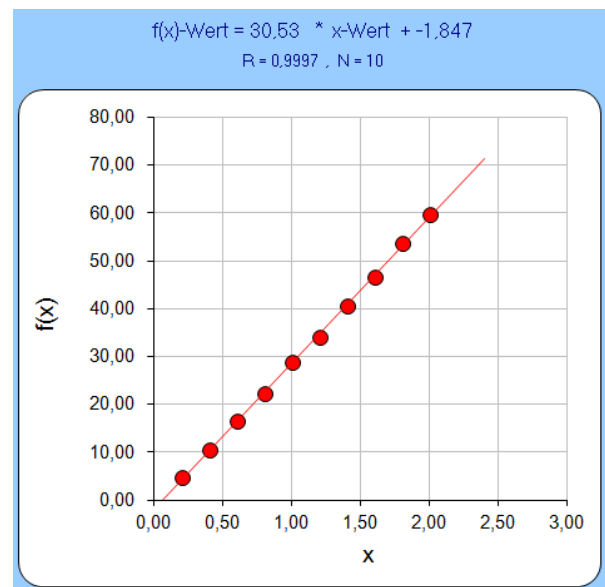
System: TOC-L CPN
Catalyst: Standard catalyst
(Al-balls covered with Pt)
Method: TN (with TNM-L)
Injection vol.: 140µl

■ 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 NO₃) stock solution.

Calibration Curve Properties						
Common Parameter Analysis Data Graph History						
Inj. Volume:						140 µl
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)						

■ 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

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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.