4. TOC special applications

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

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

The TOC parameter can be determined easily and reliably. The experienced user can control and calculate interferences that can be attributed to the matrix. Various options, kits and modules enable interference-free analyses in a wide range of applications.

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

The possibility to detect and quantify all organic compounds within a simple analytical run always leads to new, often unusual, applications. Some only seem to be useful for a one-time use while others seem to revolutionize entire analytical application areas.

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

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Application News

No. SCA-130-401

Sum parameter – Total Organic Carbon

TOC- determination in algal biomass – suspension method

The excessive global CO_2 emissions from the burning of fossil fuels (for instance in power plants) causes the search for climate-friendly uses of carbon dioxide.

One of the approaches for environmentally sound recycling is to convert the emitted CO_2 into biomass using photobioreactors.

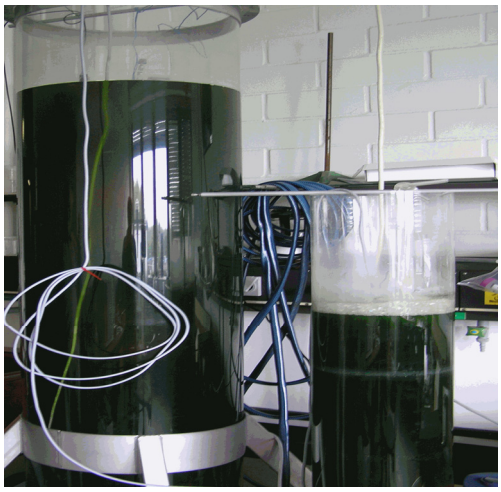
The CO_2 gas is introduced into the photobioreactor in order to be used for the growth of algae. The biomass, or algae, can be used in many different application areas: in the cosmetics industry, the construction industry, and the food segment, in agriculture as fertilizer or for energy utilization.

■ Test methods for implementation

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

■Innovative methods

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



■ TOC Measurement method

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

Information on the analysis:

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

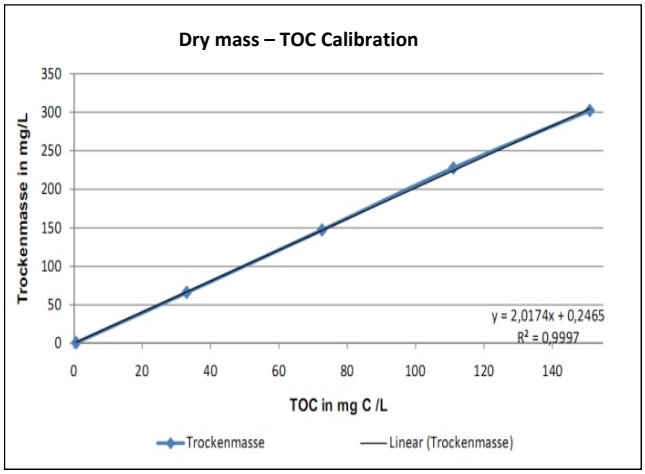
■ Sample preparation

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

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

■ Corrrelation

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



First, the algae sample is measured and the TOC is determined. Subsequently, the sample is filtered through a 0.2 µm syringe filter and measured again in the TOC analyzer to be able to distinguish between the TOC content originating from the algae and the carbon content possibly originating from the extracellular substances produced by the algae or released into the culture medium after the algae have died off. The TOC determined this way is the carbon content of the investigated algae. To draw conclusions on the dry mass yield, the percentage carbon content in the algae must be determined.

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

■ Recommended analyzer / Configuration

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

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Application News

No. SCA-130-402

Sum parameter – Total Organic Carbon

TOC-determination in liquid manure and fermentation fluids – suspension method

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

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

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

Fig. Experimental setup to generate bio gas in the laboratory

■ Efficiency

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

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

■ Innovative methods

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

Fig. Homogenisation of the suspension

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

The advantage of this alternative method lies in its suitability for automation. This way, many samples can be processed automatically in sequence.
With the possibility of multiple injections, the method also offers statistical reliability. In the muffle furnace, a combusted weighed sample yields an ODM value. The suspensions are generally analyzed at least four times to establish a mean value.

■NPOC-Determination

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

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

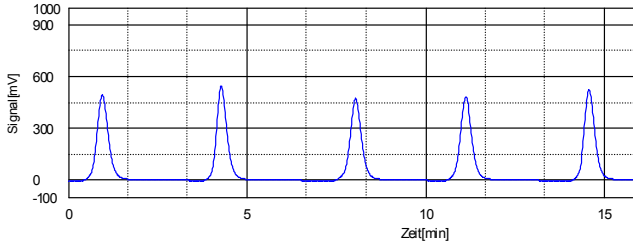

Fig. NPOC-Peaks of suspension

■ TN_b-Determination

The TOC determination using catalytic combustion oxidation allows the simultaneous measurement of the total bound nitrogen (TN_b), since, in addition to the carbon dioxide from organic substances, NO is formed from nitrogen-containing compounds. For the conversion of NO to NO_2, the measuring gas ozone was fed to the chemiluminescence detector connected in-series. The photons emitted during this reaction are detected and are used in the calculation of the TN_b value. Nitrogen compounds also play an important role when it comes to liquid manure.

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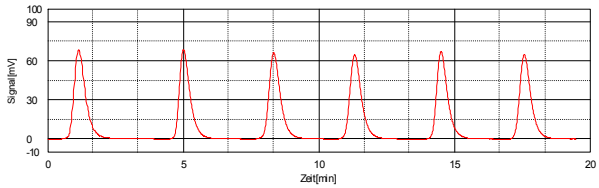

Fig.4: Peak graphs of TN-determination

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

Liquid manure (dried and powdered)	TN_b [mass.-%]	RSD [%]
Sample 1	1,84	1,5
Sample 1	1,80	0,9
Sample 2	1,76	2,2
Sample 2	1,68	1,4

■ Conclusion

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

■ Recommended Analyzer / Configuration

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

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Application News

Sum parameter – Total Organic Carbon

Carbon dioxide determination in beer

No. SCA-130-403

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

The CO_2 content of a beer affects the threshold values for various fragrance and aroma components. In addition, bottling under CO_2 increases the shelf life of beer..

In the manual of the 'central- European brewery technological analysis commission)' (MEBAK) various methods for the determination of CO_2 are listed. These are generally based on manometric or titrimetric method, or they are methods that use specialized detectors.

Disadvantages of these methods are often the lack of selectivity for CO_2 (other gases or substances are also determined), high expenditure in terms of personnel and time, and the lack of possibilities for automation.

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

■ Innovative methods

In this method, the sample (beer) is directly placed in a 40 mL autosampler vial. 5 mL of a 32% NaOH solution was added to the autosampler vial to preserve the CO_2.

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

Preservation step:

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

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

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

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

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

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

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

■ Advantages of this method

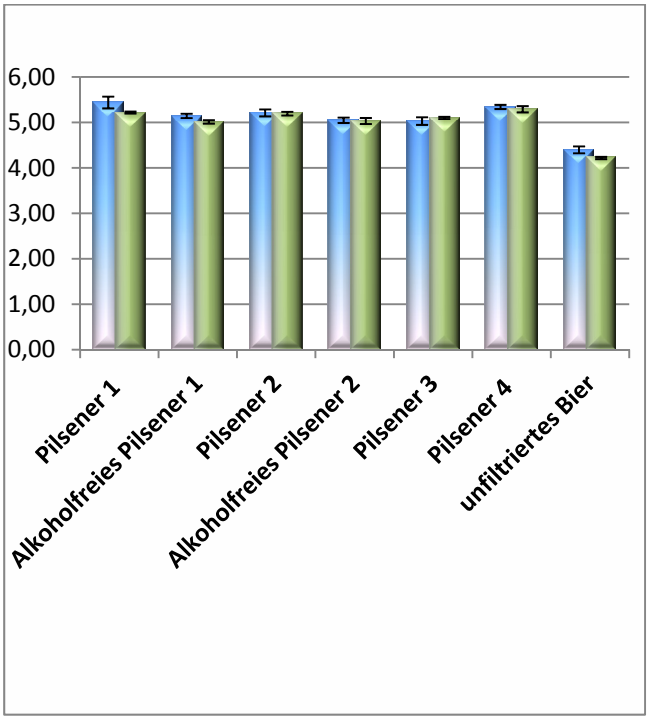
- can be automated to a high degree
- fast
- good reproducibility and high accuracy (precision)
- multiple determinations from one sample is possible
- effortless calibration
- simple operation
- highly specific

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

Another sample preparation variant is to be carried out during the determination of carbon dioxide in bottled or canned beer. In this step, 5 mL of a 32% solution of NaOH was directly added to the freshly opened bottle or can for preservation.

■ Comparison of the methods

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



■ Recommended Analyzer / Configuration

TOC-L CPH
ASI-L (40ml)