SHIMADZU
Excellence in Science

4. TOC special applications

4. TOC special applications

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

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

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

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

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

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

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.

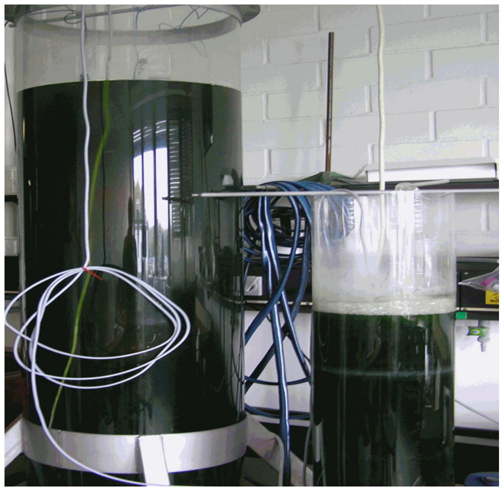
The CO_2 gas is introduced into the photobioreactor in order to be used for the growth of algae. The biomass, or algae, can be used in many different application areas: in the cosmetics industry, the construction industry, and the food segment, in agriculture as fertilizer or for energy utilization.

■ 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

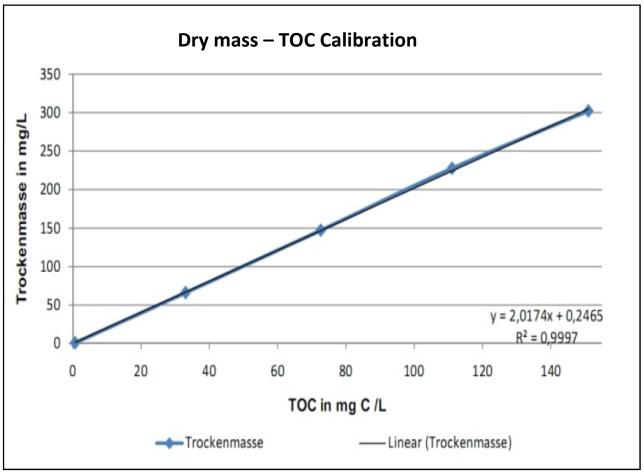
■ Sample preparation

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

SHIMADZU
Excellence in Science

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

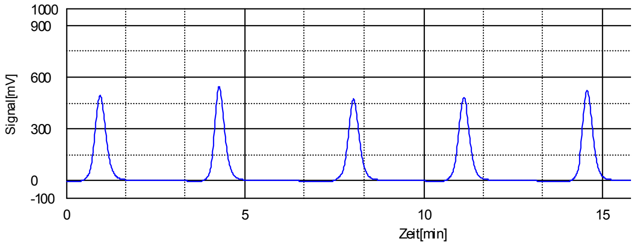


Fig. NPOC-Peaks of suspension

■ 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.

.

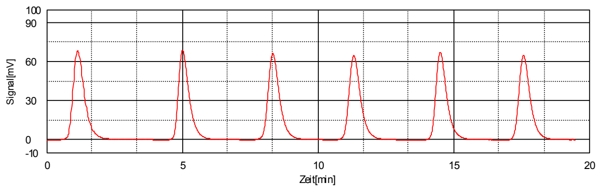


Fig.4: Peak graphs of TN-determination

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.

SHIMADZU
Excellence in Science

Application News

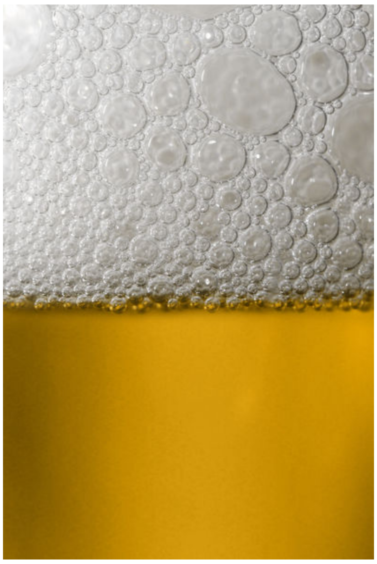
Sum parameter – Total Organic Carbon

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

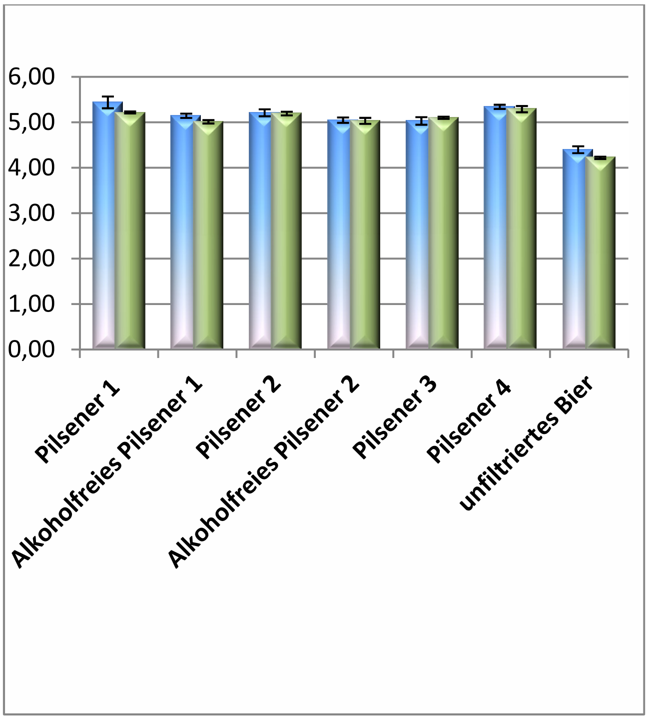
- can be automated to a high degree
- fast
- good reproducibility and high accuracy (precision)
- multiple determinations from one sample is possible
- effortless calibration
- simple operation
- highly specific

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)

SHIMADZU
Excellence in Science

Application News

No. SCA-130-404

Sum parameters – Total Organic Carbon

TOC-determination in water for the production of beverages

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

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

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

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

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

▪ Analytical method

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

▪ Calibration

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

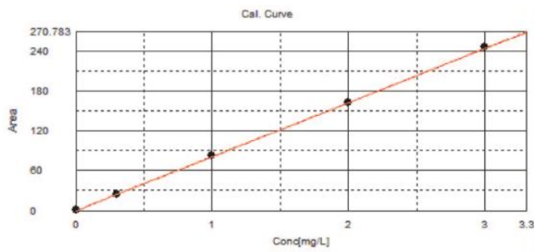


Fig.1: 5-point calibration in range 0 to 3mg/L

▪ Method parameters

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

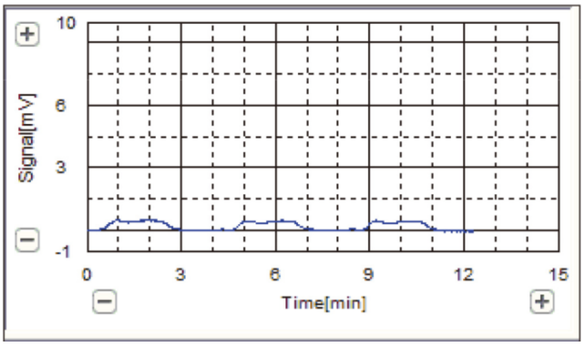


Fig.2: 3 NPOC-Injections of spring water

▪ Results

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

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

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

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

▪ Recommended instrument / configuration

TOC-L $_{CPH}$

ASI-L

SHIMADZU

Shimadzu Europa GmbH

www.shimadzu.eu

SHIMADZU
Excellence in Science

Application News

No.O49

Total Organic Carbon Analysis

Monitoring of Algae Growth by TOC Measurement

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

T. Iharada, M. Tanaka

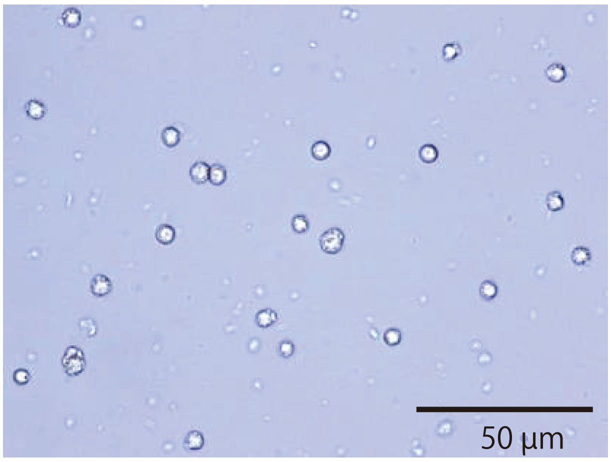


Fig. 1 Algae

Analytical Method

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

Measurement Results

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

<Measurement Conditions>

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

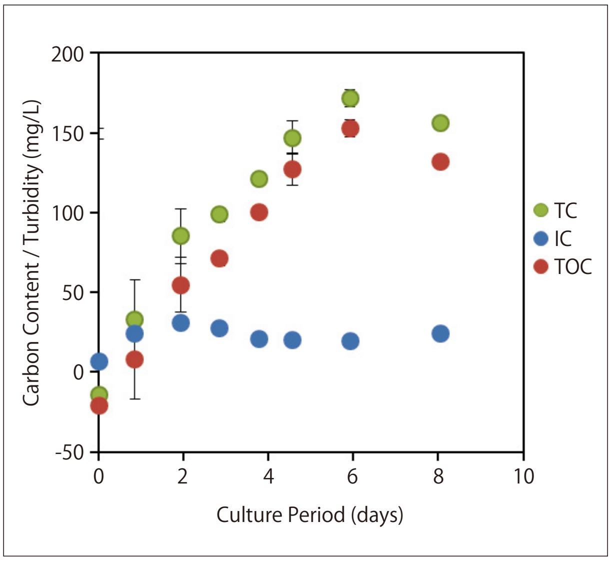


Fig. 2 Changes in TC, IC, TOC Quantity in Microalgae Cells (Conversion value per turbidity unit)

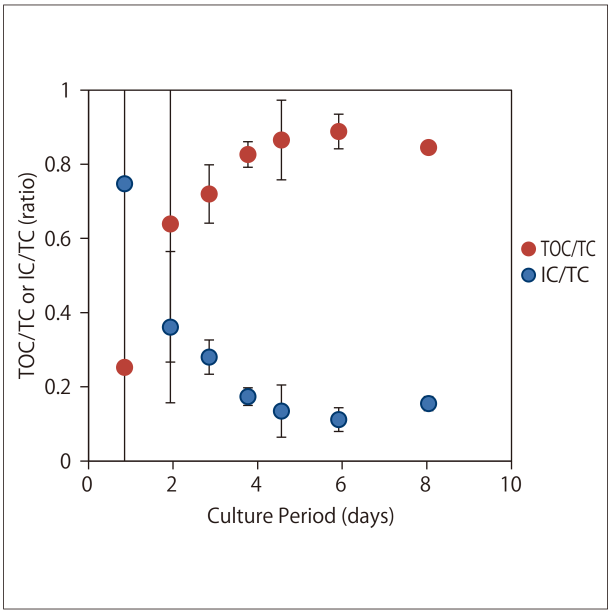


Fig. 3 Changes in TOC/TC and IC/TC in Microalgae Cells

Shimadzu TOC-L Series Total Organic Carbon Analyzer

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

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

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

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

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

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

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

First Edition: Apl. 2014

SHIMADZU
Shimadzu Corporation
www.shimadzu.com/an/

SHIMADZU
Excellence in Science

Application News

Total Organic Carbon Analysis

Characterization of Algae by TOC Measurement

No.O50

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

T. Iharada, M. Tanaka

■ Analytical Method

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

<Measurement Conditions>

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

■ Measurement Results

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

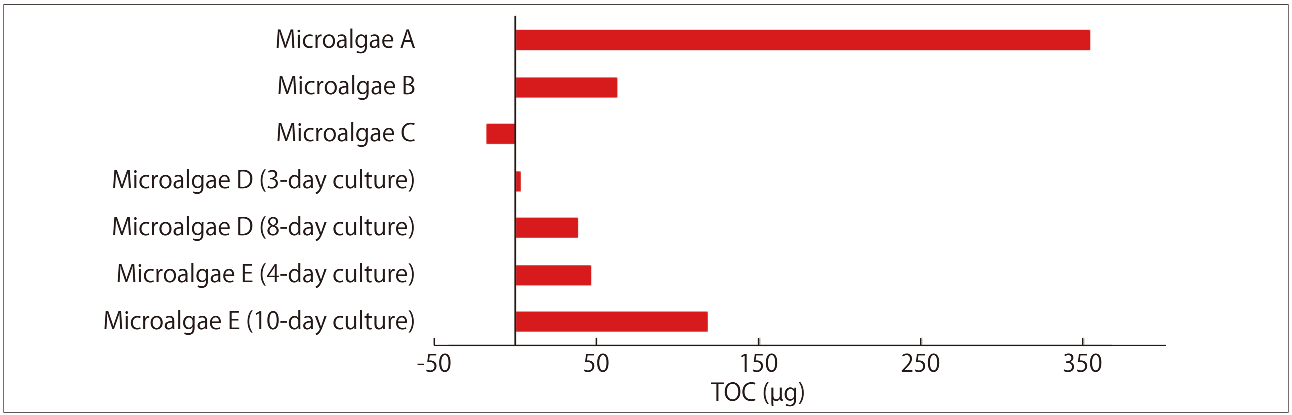


Fig. 1 TOC/OD in Culture (Conversion value per turbidity unit)

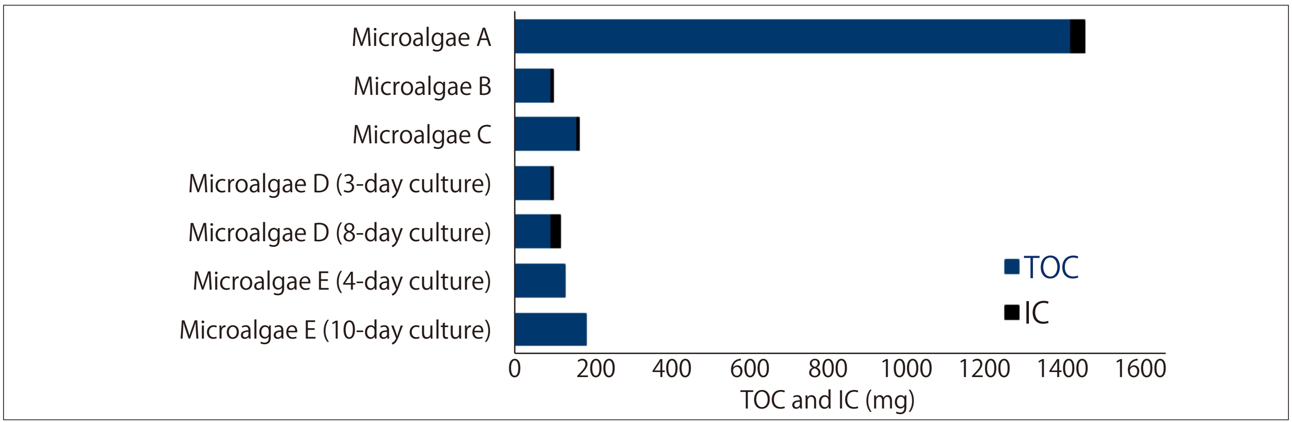


Fig. 2 TOC and IC/OD in Cell (Conversion value per turbidity unit)

Shimadzu TOC-L Series Total Organic Carbon Analyzer

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

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

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

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

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

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

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

First Edition: Apl. 2014

Application News

No. SCA-130-407

Sum parameters – Total Organic Carbon

Cleaning validation in the food and consumables industries

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

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

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

■ IFS Food

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

■ Suitable methods

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

■ Parameters

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

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

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

■ Sampling

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

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

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

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

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

■ Measurement parameters

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

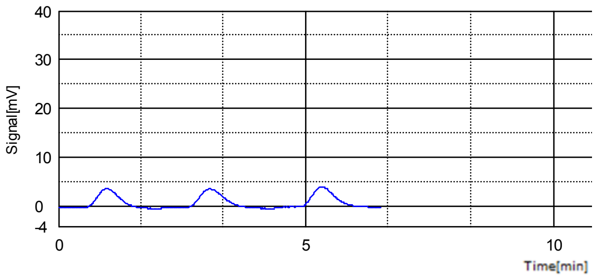


Figure: 3 Injections of the final rinse.

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

■ Recommended analyzer / configuration

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

Application News

No. SCA-130-408

Sum parameters – Total Organic Carbon

TN_b Determination

For the risk assessment of allergen carryover in food production

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

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

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

▪ TN_b / TOC - Determination

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

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

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

▪ Tests with foods containing allergens

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

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

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

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

▪ Conclusion

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

▪ Recommended analyzer / configuration

TOC-L $_{CPX}$
TNM-L
ASI-L

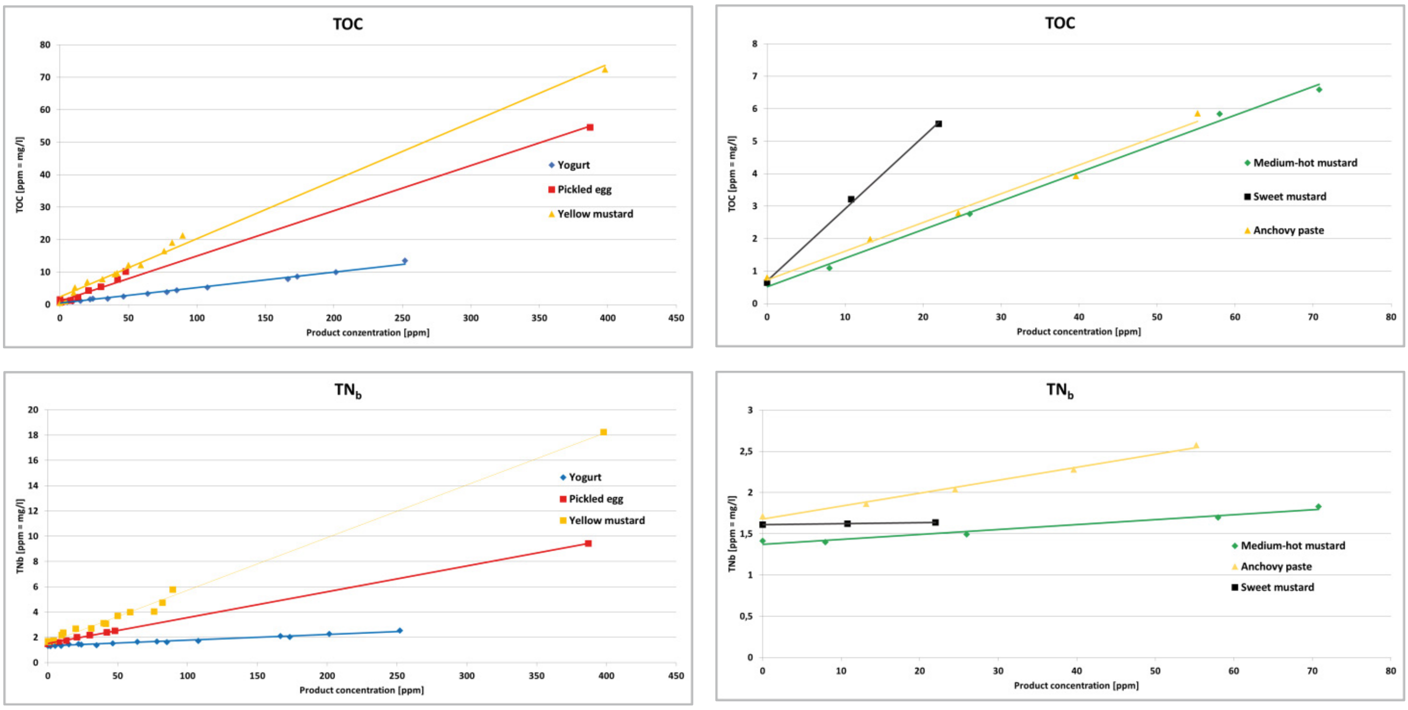


Fig.: „TOC and TN_b-calibrations“ of different foods in various concentrations