C391-E100

SHIMADZU
Excellence in Science

TOC
TALK LETTER

Vol. 1

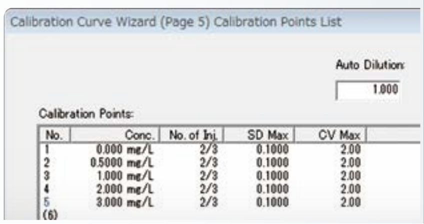
Accuracy Control Function For More Reliable Measurements

—Introducing the Accuracy Control Function—

The TOC-Control L software accuracy control function offers a solution to customers that require more reliable measurement results. This function enables the user to confirm the reliability of measured results by analyzing samples of known concentrations (accuracy control samples) during consecutive analysis of multiple samples using an autosampler.
If the difference between the known concentration and measured concentration of the accuracy control sample is outside control criteria, recalibration is automatically performed and the unknown samples are reanalyzed. The control criteria that trigger repeat analysis can be set as desired.

Setting Multiple Calibration Curves

A maximum of 10 calibration curves can be created.


Calibration Curve Wizard (Page 5) Calibration Points List

Auto Dilution: 1.000

Calibration Points:

No.	Conc.	No. of Inj.	SD Max	CV Max
1	0.000 mg/L	2/3	0.1000	2.00
2	0.5000 mg/L	2/3	0.1000	2.00
3	1.000 mg/L	2/3	0.1000	2.00
4	2.000 mg/L	2/3	0.1000	2.00
5	3.000 mg/L	2/3	0.1000	2.00
(6)				

Controlling and Correcting Measurement Accuracy

If the measured result exceeds the set upper or lower limit (measurement accuracy), recalibration is automatically performed and the previously measured unknown samples are reanalyzed.

Setting the measurement accuracy control concentration
(when using 2.00 mg/L accuracy control samples)

Lower limit: **1.60 mg/L** Upper limit: **2.40 mg/L**
→Limits can be adjusted for more rigorous accuracy control.

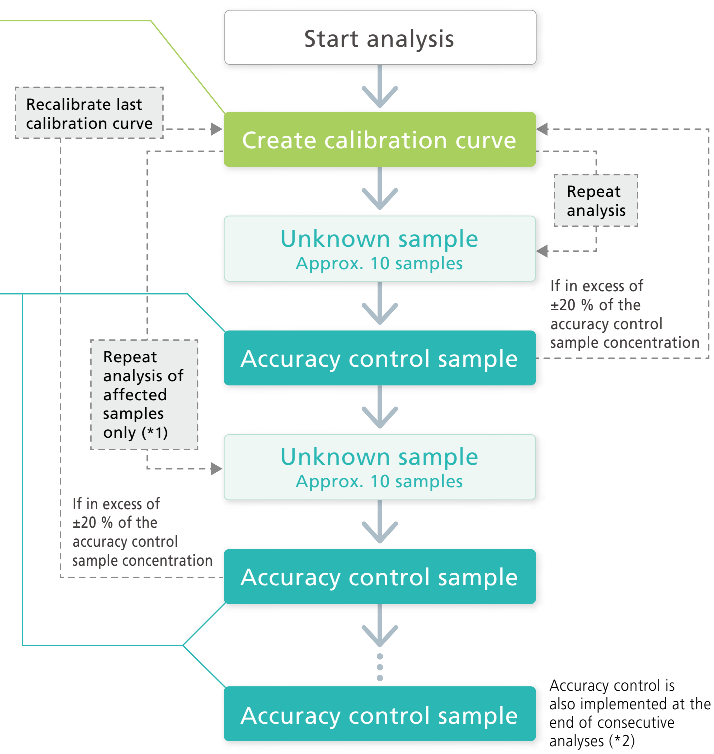
If the upper or lower limit is exceeded

Action when the failure event occurs the first time:
Repeat (from last control or calibration)

Action when the failure event occurs the second time:
Stop (whole sample run)

* Setting the same conditions as shown in this page will create suitable conditions for measurement accuracy control.

By using a registered schedule file, once vials have been prepared, analysis can be started simply by pressing the [Start] button.

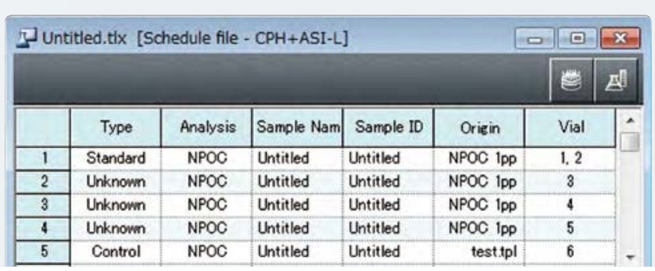


*1 When a result does not meet the control criteria, all unknown samples analyzed after the last accuracy control sample measurement are reanalyzed.
*2 By measuring the accuracy control sample at the end of consecutive analyses, accuracy control is maintained until the final sample.

Schedule File Registration

Measurements of multiple samples with specified measurement conditions or vial numbers can be registered as a schedule file to facilitate routine measurements.

* Sample types shown include:
Standard = sample for calibration curve creation, Unknown = unknown sample, Control = sample used for accuracy control.


Untitled.tlx [Schedule file - CPH+ASI-L]

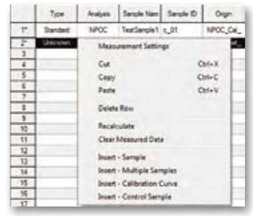
	Type	Analysis	Sample Nam	Sample ID	Origin	Vial
1	Standard	NPOC	Untitled	Untitled	NPOC 1pp	1, 2
2	Unknown	NPOC	Untitled	Untitled	NPOC 1pp	3
3	Unknown	NPOC	Untitled	Untitled	NPOC 1pp	4
4	Unknown	NPOC	Untitled	Untitled	NPOC 1pp	5
5	Control	NPOC	Untitled	Untitled	test.tpl	6

The TOC-Control L software has a user-friendly interface that makes it easy to set the analytical conditions used for accuracy control.

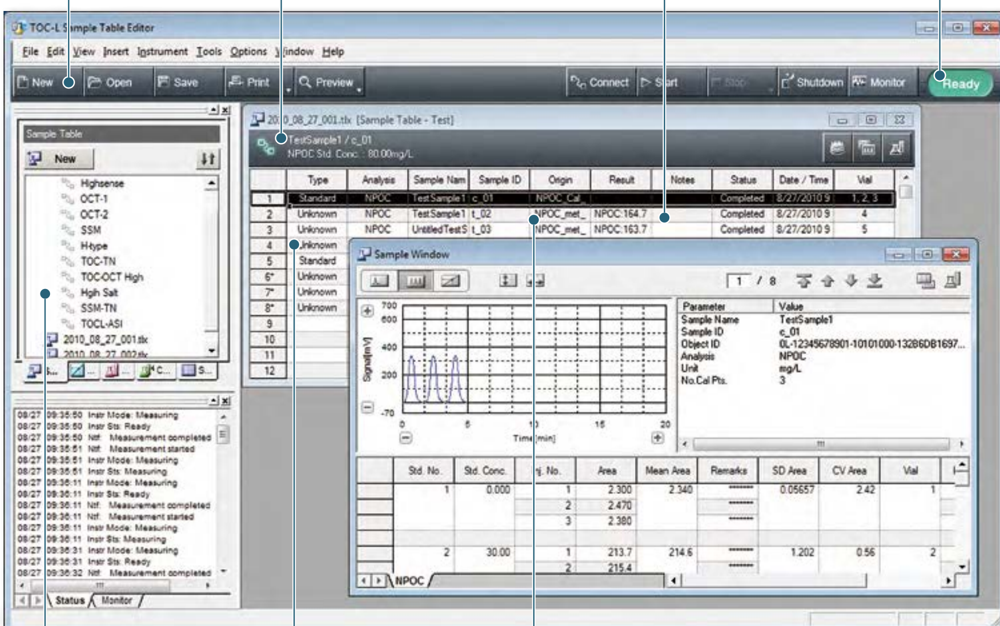
Icons and function names shown on large buttons

User-friendly display of the name, ID, and measured results for selected samples, each in specific columns

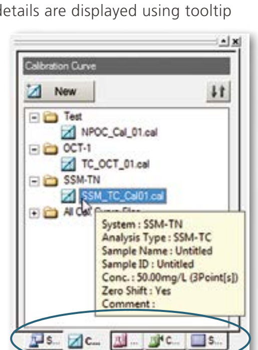
Operations are accessed by right-clicking on the table



User-friendly display of instrument status using text and color

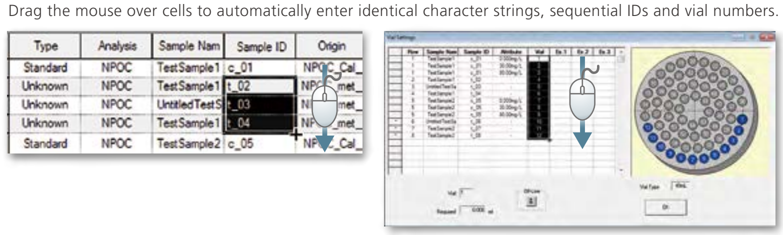


- Files are listed by type
- Files can be sorted by file name and date created
- File details are displayed using tooltip

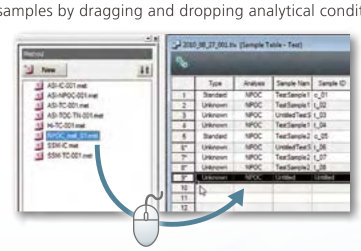


Classification by type

Drag the mouse over cells to automatically enter identical character strings, sequential IDs and vial numbers.



Insert samples by dragging and dropping analytical condition files.



Yuichi Masuda
Environmental Business Unit, Analytical & Measuring Instruments Division

Microalgae Measurements

Biomass fuels are attracting more attention because of the problems caused by global warming due to the use of fossil fuels. Microalgae have some clear advantages over other biomass fuels in that oil production by microalgae does not compete with food production. Biofuel productivity is higher with microalgae than with other biofuel sources considering time and area used, and there are many potential options in terms of land that can be used to cultivate microalgae. As for the practical use of microalgal biomass, various studies are being undertaken into each step of microalgae production, including strain selection, breed improvement, cultivation, harvesting, oil extraction and purification. Shimadzu's TOC-L series of combustion-based total organic carbon analyzers have an organic material oxidating power strong enough to completely oxidize microalgae cell suspensions such as those found in culture solution, and enable measurement of their total organic carbon content.

The following presents an example of a unique application in which the TOC-L_{CPH} total organic carbon analyzer is used to measure directly, without pretreatment, the TOC content in a suspended culture of microalgae cells.

1. Tracking the Microalgae Growth Process

1-1. Analytical Method

Microalgae were cultured for eight days, and on each day from day 1 of culture, a sample of culture solution containing suspended microalgae cells was taken, named Sample 1, and analyzed to measure the TOC content. This Sample 1 was also centrifuged to remove microalgae cells from suspension by sedimentation, and the remaining culture solution supernatant named Sample 2 was analyzed to measure its TOC content. The TOC content of the organic material present in microalgae cells was then calculated from the difference in TOC content in Sample 1 and Sample 2. The turbidity of Sample 1 was also measured, and the result used as an index of cell mass.

A microscopic image of the microalgae cells in Sample 1 is shown in Fig. 1.

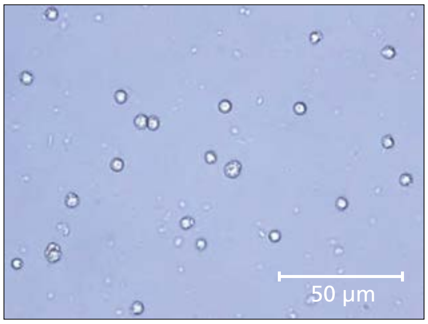


Fig. 1 Microalgae Cells

1-2. Measurement Results

The measurement results for total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) present per unit of cell mass during the period of culture is shown in Fig. 2. The proportions of TOC and IC present in the microalgae cells are also shown in Fig. 3. These results can be used to obtain information on how TC, IC and TOC levels in the microalgae cells change over time during the culture process.

Establishing culture conditions is an essential part of the practical realization of microalgal biomass production, and these results show that a TOC analyzer can be used to obtain information related to the carbon balance of a microalgae cell culture.

Analytical conditions

Instrument	Shimadzu TOC-L_{CPH} total organic carbon analyzer
Catalyst	Standard catalyst
Measured items	TOC (TC-IC)
Calibration curve	One-point calibration curve obtained from an aqueous solution of 1000 mgC/L potassium hydrogen phthalate
Sample 1	Culture solution containing suspended microalgae cells
Sample 2	Culture solution after removal of microalgae cells by centrifugal sedimentation
Sampling method	Sample 1 was harvested during agitation with a magnetic stirrer

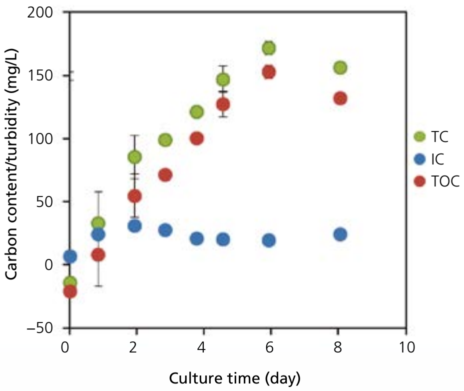


Fig. 2 Changes in TC, IC and TOC Content of Microalgae Cells (conversion value per turbidity unit)

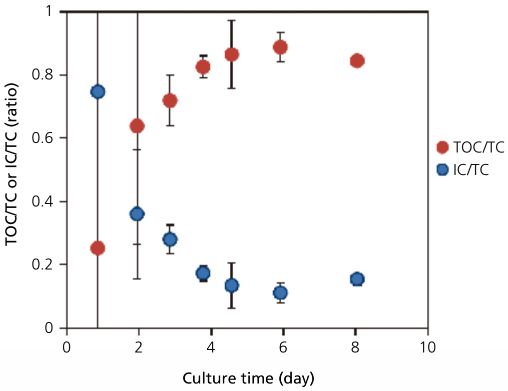


Fig. 3 Changes in TOC/TC and IC/TC in Microalgae Cells

2. Microalgae Characterization

2-1. Analytical Method

Five types of microalgae (A through E) were cultured for 3 to 14 days. At the start of culture, several days after starting culture, and at the end of culture a sample of culture solution containing suspended microalgae cells was taken, named Sample 1, and analyzed to measure the TOC content. This Sample 1 was also filtered to remove microalgae cells, and the remaining culture solution filtrate named Sample 2 was analyzed to measure its TOC content. The TOC content of the organic material present in each microalgae cell was then calculated from the difference in TOC content in Sample 1 and Sample 2. The turbidity of Sample 1 was also measured, and the result used as an index of cell mass.

Analytical conditions

Instrument	Shimadzu TOC-L_{CPH} total organic carbon analyzer
Catalyst	Standard catalyst
Measured items	TOC (TC-IC)
Calibration curve	One-point calibration curve obtained from an aqueous solution of 1000 mgC/L potassium hydrogen phthalate
Sample 1	Culture solution containing suspended microalgae cells
Sample 2	Culture solution after removal of microalgae cells by filtration
Sampling method	Sample 1 was harvested during agitation with a magnetic stirrer

2-2. Measurement Results

The increase in TC, TOC and IC in the five types of microalgae cells and their culture solutions are shown in Fig. 4 and Fig. 5.
The results show that organic material take-up and release by the cells differed depending on the microalgae type and number of culture days. The results also suggested that for microalgae that form a calcium carbonate shell, information on shell formation can be obtained from IC measurement.
These results show that TOC analysis can be used for microalgae screening and to investigate culture conditions.

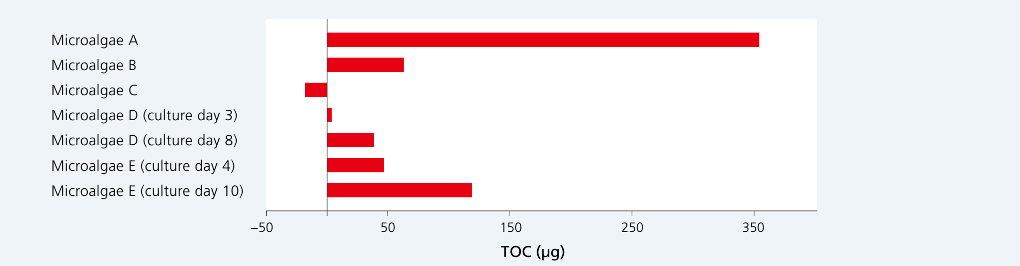


Fig. 4 Increase in TOC Content of Culture Solution (conversion value per turbidity unit)

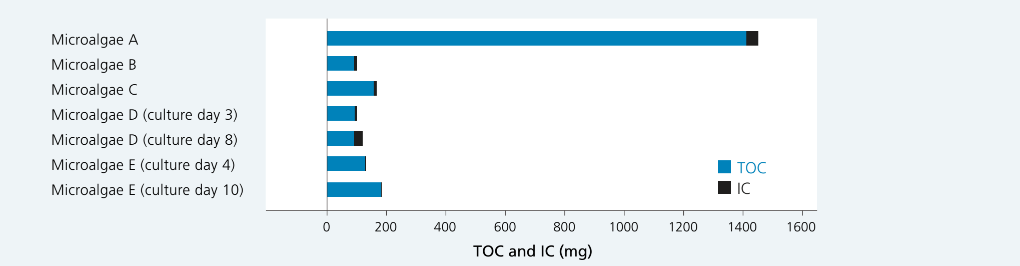


Fig. 5 Increase in TOC and IC Content of Cells (conversion value per turbidity unit)

3. Conclusion

TOC-L total organic carbon analyzers can be used to analyze microalgae suspended in culture solution without pretreatment, and can therefore be utilized for the following applications in microalgal research.

- Obtain information related to the properties and physiological state of microalgae.
- Understand how cell properties change over time during culture, and how cell properties change in light and dark conditions.
- Understand quantitatively the carbon balance and nitrogen balance of culture systems.

* The data in this article were provided by Professor Shiraiwa's research laboratory at the University of Tsukuba.

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The Basics of TOC Measurement

IC Measurement and IC Removal

Total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) have the following relationship.

$$TC = TOC + IC$$

Based on the fact that only TC and IC can be measured directly out of these three parameters, the two following methods can be used to measure TOC.

(1) Calculate TOC from the difference between measured TC and IC. (TOC = TC - IC)
(2) Remove IC by pretreatment, and then calculate TOC from the measured TC. (TOC = TC)

Method (1) measures IC and method (2) removes IC. This article explains the principles for these two methods.
The IC component of TOC analysis refers to the total quantity of carbon (shown in red in the equation below) present as dissolved carbon dioxide, bicarbonate ions and carbonate ions[*1]. As shown in the equation below, these carbon species are present in water in an equilibrium state, and this equilibrium is driven by sample pH.

$$\color{red}{C}O_2 + H_2O \Leftrightarrow H\color{red}{C}O_3^- + H^+ \Leftrightarrow \color{red}{C}O_3^{2-} + 2H^+$$

When pH decreases, equilibrium shifts to the left in the above equation, and at pH 3 or below almost all IC is present as dissolved carbon dioxide. At this state of equilibrium, carbon dioxide is present in water as a dissolved gas, and can be driven out of the sample simply by purging the sample with a gas that contains no CO_2. Thus, the IC of a sample can be extracted by adding acid to reduce its pH to 3 or below, and then purging the sample with a gas that contains no CO_2.

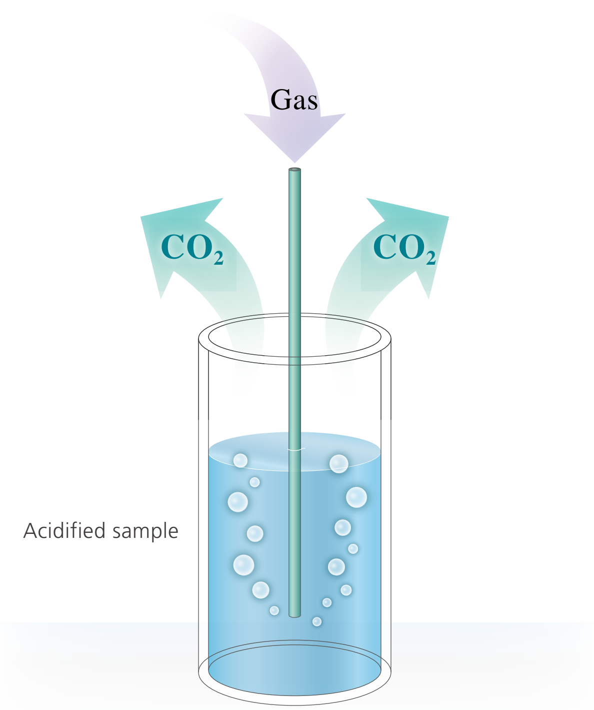

Fig. 1 IC Extraction

IC measurement involves measuring the amount of CO_2 extracted during purging, while IC removal involves simply disposing of the purged CO_2. In other words, the procedures for IC measurement and IC removal are based on the same principle.
The efficiency of IC extraction is affected by the degree of gas-liquid contact during purging. IC extraction efficiency will be good as long as pH is 3 or below, while adding more acid than needed to reach this pH has no supplementary effect.
Method (2) of calculating TOC is called the NPOC method, and the TOC content value measured called the NPOC value. NPOC stands for non-purgeable organic carbon. Why method (2) is called the NPOC method is explained below. During the purging process of IC removal, the sample is stripped off all or some of its purgeable organic carbon (POC), which can result in a lower measured TOC value than the actual TOC in the sample (Fig. 2). This problem almost never arises since it is rare for a sample used in TOC measurement to contain a significant amount of POC. However, method (2) is called the NPOC method based on the idea that this problem can occur in principle.

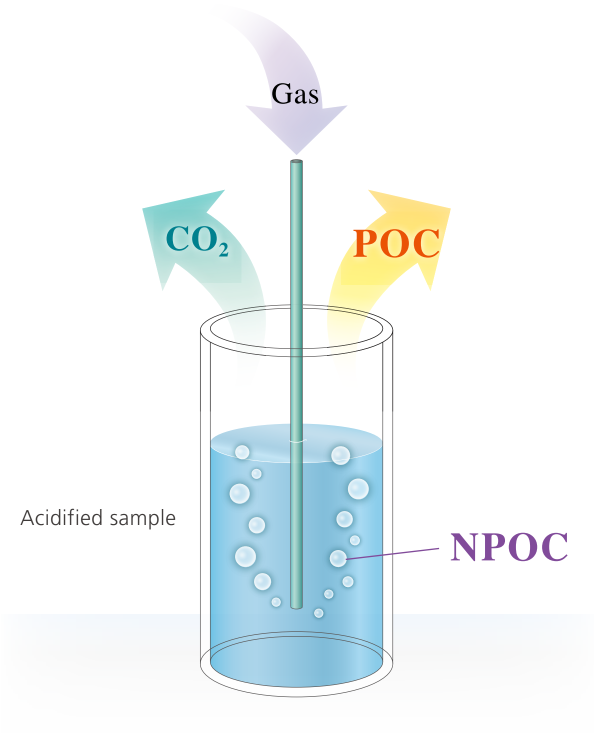

Fig. 2 Loss of POC During Purging

*1 In chemistry, the carbon found in elemental carbon particles (soot), carbide, cyanide ions, cyanate ions and thiocyanate ions are categorized as IC, but for the purpose of TOC measurement, the carbon present in these forms is measured as TOC.

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TOC-L

TOTAL ORGANIC CARBON ANALYZER

Applications in a variety of fields

Process Control

- ·Effluent treatment process control
- ·Ultrapure water recycling and re-purification processes

Quality Control

- ·Water supply equipment
- ·Electronic components
- ·Aluminum foil
- ·Raw materials

Investigations and Experimental Research

- ·Global environment, eutrophication, river water, lakes and marshes, underground water, and sea water
- ·Soil, sludge, and sediments
- ·Biodegradable plastics and cement secondary products

Water Quality Control

- ·Tap water
- ·Ultrapure water
- ·Effluent and raw wastewater
- ·Swimming pool and spa water
- ·Boiler water and water from industrial processes

Pharmaceutical Manufacturing

- ·Pharmaceutical water control
- ·Evaluation of cleaning effectiveness

(Cleaning validation)

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