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Application News

TOC-L Total Organic Carbon Analyzer + SSM-5000A Solid Sample Combustion Unit

Measurement of Total Organic Carbon in Salt-Containing Sediments

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User Benefits

- By performing a desalination process, it is possible to measure sediment samples containing salts.
- The measurement time for both TC and IC is approximately 6 to 8 minutes per analysis, allowing for rapid measurement.
- A single system enables TOC measurement for both liquid and solid samples.

■ Introduction

Sediments refer to the surface-layer deposits accumulated at the bottoms of water bodies such as lakes, seas, and rivers. The organic matter in sediments plays various roles in aquatic ecosystems, including nutrient supply and pollutant adsorption. Therefore, measuring the organic matter content in sediments is crucial for understanding sediment characteristics and is an essential process for environmental management and ecosystem protection. Total organic carbon (TOC) measurement provides a quantitative evaluation of organic matter in sediments.

However, when directly measuring sediments that contain salts, concerns arise regarding the influence of the salts on measurement values, as well as potential corrosion of the detector and other impacts on the equipment. To prevent these issues, a desalination process is required to reduce the salt concentration before measurement.

This article explores sample pretreatment methods, including desalination, for salt-containing sediment samples and presents an example of TOC measurement in such sediments.

■ TOC Solid Sample Measurement System

The TOC solid sample measurement system (Fig. 1), consisting of a TOC-L combustion-type total organic carbon analyzer and an SSM-5000A solid sample combustion unit, quantifies carbon by detecting carbon dioxide (CO_2) generated through combustion oxidation or acid decomposition of carbonates.

For total carbon (TC) measurement, the sample is combusted at 900 °C in an oxygen atmosphere, allowing for the quantification of all carbon content within the sample. For inorganic carbon (IC) measurement, the sample is acidified with phosphoric acid and heated to 200 °C, extracting CO_2 from carbonate-based carbon. TOC content is then determined as the difference between TC and IC values.

The analysis is simple and quick—the sample is weighed into a sample boat and introduced into the system. To ensure accurate results, samples should be finely ground, as large particles may cause longer reaction times or incomplete reactions.

Additionally, the TOC-L analyzer (Fig. 1, left) can also measure liquid samples (TOC, TC, IC) simply by adjusting the software settings.

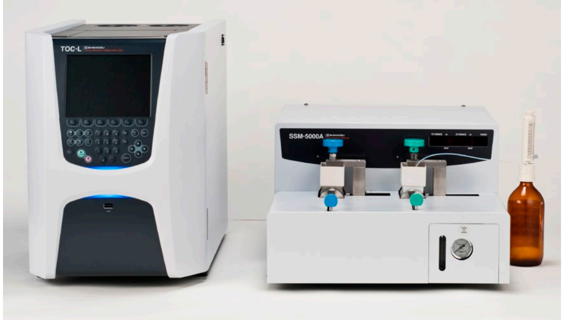

Fig. 1 TOC Solid Sample Measurement System
TOC-L Total Organic Carbon Analyzer (left) and SSM-5000A Solid Sample Combustion Unit (right)

■ Samples and Pretreatment

A sediment sample containing salts was collected from a brackish water area (with a salinity level approximately half that of seawater) and prepared for analysis. The collected sample underwent pretreatment as shown in Fig. 2 and Fig. 3 before measurement. The dried sample from Fig. 2 was used for subsequent analysis.

1. Preparation of Wet Sediment Sample (Fig. 2)

A portion of the collected sediment sample was centrifuged at 3,000 rpm for 20 minutes. After removing the supernatant, the remaining solid material was mixed to obtain a wet sediment sample.

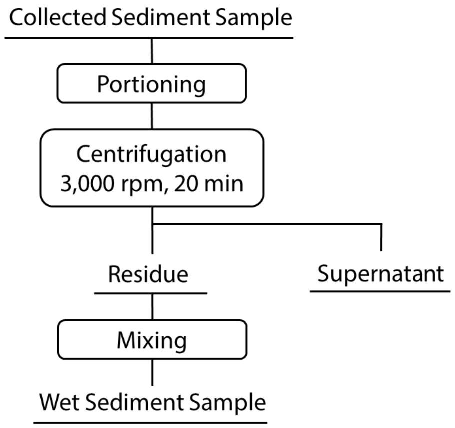

Fig. 2 Preparation of Wet Sediment Sample *1

2. Preparation of Dried Sediment Sample (Fig. 3)

A portion of the wet sediment sample was spread evenly on a glass dish and dried in an oven at 105 to 110 °C for approximately 2 hours. The dried sample was then lightly crushed and loosened using an agate mortar and pestle, resulting in the dried sediment sample.

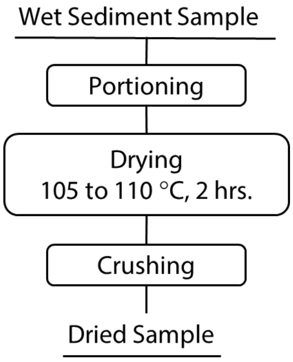

Fig. 3 Preparation of Dried Sediment Sample *1

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*1 Pretreatment based on the 'Sediment Survey Method' [1] published by the Water and Air Environment Bureau of the Ministry of the Environment, Japan, with some steps omitted.

3. Desalination Treatment of Sediment (Fig. 4)

When measuring TC in salt-containing samples using a solid sample combustion unit, mist formation can occur, potentially damaging consumable components such as combustion tubes and making measurement impossible. Therefore, it is necessary to perform desalination treatment to reduce the salt concentration in the sample. In this process, two key considerations are required: (1) Selection of the desalination method. (2) Evaluation of TOC loss due to desalination and necessary correction calculations.

To lower the salt concentration in the sediment sample, desalination was performed following the procedure shown in Fig. 4. An appropriate amount of pure water was added to the dried sample, followed by centrifugation at 2,500 rpm for 10 minutes.

By analyzing the supernatant, changes in chlorine and TOC concentration in the liquid due to desalination treatment were assessed. The solid residue was then dried in an oven at 105 to 110 °C for approximately 2 hours before being used for solid sample measurement.

In this study, desalination treatment was repeated multiple times to evaluate its effectiveness and determine the optimal number of treatments.

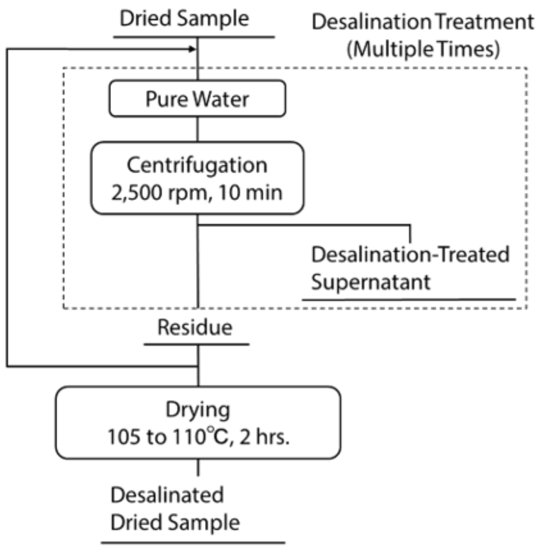


Fig. 4 Desalination Treatment of Sediment

■ Analysis Method

For solid samples such as sediments, TOC content was determined using a TOC solid sample measurement system, where both TC and IC were measured, and TOC was calculated as TC - IC.

For liquid samples such as the supernatant, TOC measurement was performed using the TOC-L analyzer. The Non-Purgeable Organic Carbon (NPOC) method was used, in which the sample was acidified, IC was removed through aeration, and TOC was measured as TC = TOC. Notably, TOC analysis of liquid samples can be performed directly even for samples with salt concentration similar to seawater.

To evaluate the effectiveness of the desalination treatment, chlorine concentration in the supernatant was measured using an energy-dispersive X-ray fluorescence spectrometer (EDX-7200).

The TOC measurement conditions are shown in Tables 1 and 2.

Table 1 Measurement Conditions for Liquid Samples

Instrument	TOC-L$_{CPH}$ total organic carbon analyzer
Catalyst	TOC standard catalyst
Measurement Items	NPOC (= TOC using acidification and sparging)
Injection Volume	50 µL
Calibration Curves	TC: 2-point calibration curve with 0 and 50 mgC/L of potassium hydrogen phthalate aqueous solution

Table 2 Measurement Conditions for Solid Samples

Instrument	TOC solid sample measurement system (TOC-L$_{CPH}$ total organic carbon analyzer + SSM-5000A solid sample combustion unit)
Cell Length	Short cell
Carrier Gas	500 mL/min oxygen gas
TC Measurement Method	Combustion catalytic oxidation (TC furnace: 900 °C)
IC Measurement Method	Phosphoric acid acidification (IC furnace: 200 °C)
Measurement Items	TC, IC
Limit of Quantitation	100 µg (absolute carbon amount)
Calibration Curve	TC: One-point calibration curve using glucose powder reagent IC: One-point calibration curve using sodium carbonate powder reagent

■ Measurement Results

1. Examination of the Number of Desalination Treatments

The supernatant of the wet sample before desalination contained approximately 1.1 % chlorine. As desalination treatment was applied, the chlorine concentration in the supernatant gradually decreased. After two desalination treatments, the concentration dropped to below 200 ppm, and after three treatments, it fell to below 100 ppm.

Based on these results, two desalination treatments were performed in this analysis, as shown in Fig. 5, before measuring both liquid and solid samples. The sample weight and supernatant volume used for calculations are also shown in Fig. 5. For volume conversion, pure water and supernatant were assumed to have a density of 1, meaning their weights were directly converted to volume.

The reason why the volume of Supernatant (1) (35.7115 mL) was smaller than the amount of pure water added (40.4631 mL) is that during the first desalination treatment, some of the added pure water was absorbed by the dried sample.

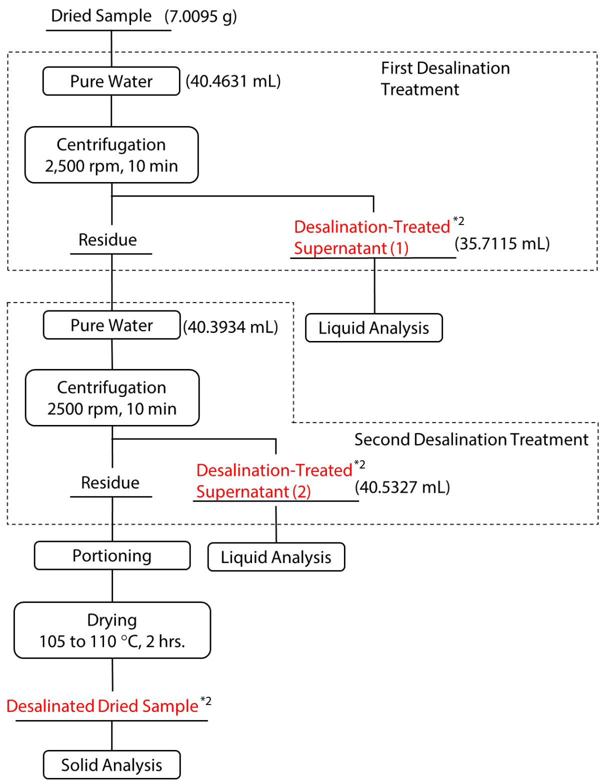


Fig. 5 Two Desalination Treatment

*2 Samples used for subsequent analysis

2. TOC Loss Due to Desalination Treatment

Table 3 shows the TOC concentration in the supernatants after desalination and the calculated TOC loss. An example of the measurement data is presented in Fig. 6.

The presence of TOC in the supernatants confirms that TOC loss occurred during the desalination process, and this TOC loss amount is used for correction calculations of the TOC content in the dried sample.

Table 3 TOC Concentration and Absolute TOC Amount in the Supernatants

Samples	Liquid Volume [mL]	TOC Conc. [mgC/L]	Abs TOC Amount [mgC]*3
Supernatant (1)	35.71	33.37	1.192
Supernatant (2)	40.53	8.686	0.3521

*3 Abs TOC Amount = Liquid Volume × TOC Conc.

3. TOC Amount in the Desalinated Dried Sample

Table 4 presents the TOC measurement results of the desalinated dried sample after two desalination treatments, with data shown in Fig. 7 and Fig. 8.

The sample had a TC concentration of 2.041 %C and an IC concentration of 0.00135 %C, resulting in a TOC concentration of 2.040 %C. The IC concentration was below the quantification limit (100 µg absolute carbon), as shown in Table 2.

The absolute TOC amount in the desalinated dried sample was calculated to be 143.0 mgC. Therefore, the TOC loss due to desalination (TOC in the supernatants) was approximately 1 % of the TOC amount in the dried sample, indicating a minor loss.

Table 4 TOC Results of Desalinated Dried Sample

Samples	TC Conc. [%C]	IC Conc. [%C]	TOC Conc. [%C]*4	Abs TOC Amount [mgC]*5
Desalinated Dried Sample	2.041	0.00135*6	2.040	143.0

*4 TOC Conc. = TC Conc. – IC Conc.

*5 Abs TOC Amount = TOC Conc. × Weight of Dried Sample
= 2.040 % × 7.0095 g
= 143.0 mgC

*6 Below the quantification limit (absolute carbon amount < 100 µg)

4. Correction Calculation of TOC Amount in Dried Sample

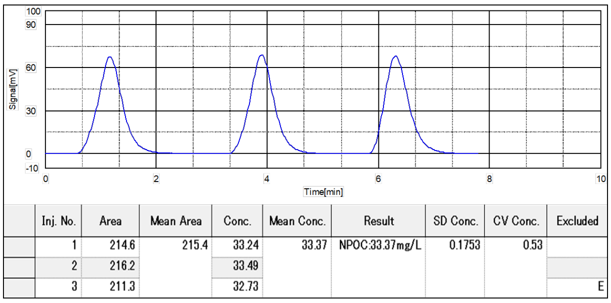
To accurately determine TOC content, the TOC amount dissolved in the supernatants, originating from the dried sediment sample, should be added. In other words, both the TOC content in the desalinated dried sample and the TOC content in the supernatants are required. The corrected calculation is shown in Table 5.

However, since the TOC loss in the supernatants is minimal compared with the total TOC in the sediment, considering the balance between measurement accuracy and practicality, it is also reasonable to directly adopt the TOC measurement value of the desalinated dried sample for practical applications.

Table 5 Correction Calculation of TOC Amount in the Dried Sample

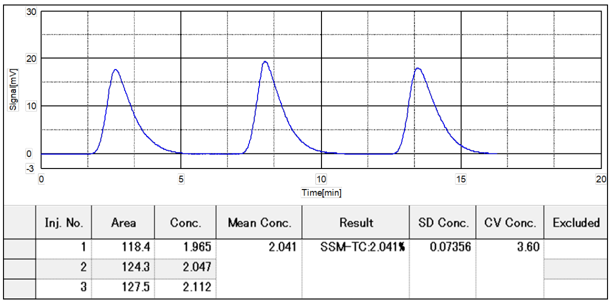
Samples	Abs TOC Amount from Dried Sample [mgC]			Weight of Dried Sample [g]	TOC Conc. [%C]*7
	Desalinated Dried Sample [mgC]	Supernatant (1) [mgC]	Supernatant (2) [mgC]		
Dried Sample	143.0	1.192	0.3521	7.0095	2.062

*7 TOC Conc. = Abs TOC Amount from Dried Sample / Weight of Dried Sample
= (143.0 + 1.192 + 0.3521) mgC / 7.0095 g × 100 %
= 2.062 %C



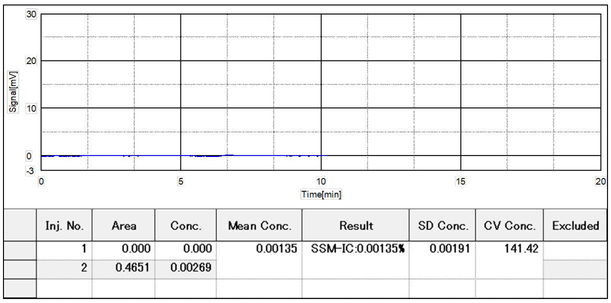
	Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
	1	214.6	215.4	33.24	33.37	NPOC:33.37mg/L	0.1753	0.53	
	2	216.2		33.49					
	3	211.3		32.73					E

Fig. 6 Desalination-Treated Supernatant (1) TOC data



	Inj. No.	Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
	1	118.4	1.965	2.041	SSM-TC:2.041%	0.07356	3.60	
	2	124.3	2.047					
	3	127.5	2.112					

Fig. 7 Desalinated Dried Sample TC data



	Inj. No.	Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
	1	0.000	0.000	0.00135	SSM-IC:0.00135%	0.00191	141.42	
	2	0.4651	0.00269					

Fig. 8 Desalinated Dried Sample IC data

■ Conclusion

This study examined appropriate pretreatment and desalination methods for TOC measurement of salt-containing sediment samples and determined the TOC values.

The results confirmed that TOC loss occurred in the supernatants during desalination. To accurately determine TOC content, a correction calculation was performed by adding the TOC from both the supernatants and the desalinated dried sample.

For the sediment sample used in this study, desalination by adding pure water and performing centrifugation proved to be an effective method. Applying the demonstrated desalination process enabled TOC measurement without salt interference. However, depending on sample properties and salt concentration, desalination conditions may require further optimization. (For salt-containing samples, the replacement interval for the detector and cell may be shorter than for normal samples.)

This study suggests that the TOC solid sample measurement system is effective for TOC measurement in sediments. Furthermore, since the system allows for both liquid and solid TOC measurements by simply adjusting the software settings, it has great potential for applications in aquatic ecosystem studies.

<References>

1) Sediment Survey Method (August 2012, Ministry of the Environment, Water and Air Environment Bureau, Japan).

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