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Application News

Total Organic Carbon Analyzer

Determination of Water-Extractable Total Organic Carbon Content in Recycled Black Mass

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User Benefits

- Measurement of the water-extractable TOC content in recycled black mass is possible.
- Using the NPOC method, TOC measurement can be simplified thanks to reduced preprocessing.
- Utilizing the ASI-L auto sampler enables multiple samples to be measured automatically.

■ Introduction

Black mass is a concentrated powder created during the recycling of lithium-ion batteries. It contains valuable metals such as cobalt and nickel, which are cathode active materials, as well as graphite, which is an anode active material. Since black mass contains these valuable metals, its recycling and reuse significantly contribute to reducing environmental impact and promoting the efficient utilization of resources.

Black mass may contain organic substances derived from used batteries that serve as raw materials, as well as organic substances from the environmental sources introduced during storage and transportation. These organic substances can leach into water or acidic solutions, which may adversely affect the refining process. This not only results in poor-quality recycled materials but also leaves residual organic substances in the waste liquids, potentially causing environmental pollution. Therefore, it is essential to quantify the total amount of organic substances contained in black mass. The amount of these organic substances can be evaluated as total organic carbon (TOC).

In China, one of the major importing countries of black mass, the evaluation of water-extractable TOC in black mass is regulated under the Chinese National Standard GB/T 45203-2024.1) According to this standard, TOC is measured using a total organic carbon analyzer based on the combustion oxidation method with non-dispersive infrared (NDIR) detection.

This article provides an example of measuring water-extractable TOC in black mass using the Shimadzu TOC-L analyzer, a total organic carbon analyzer that uses the combustion oxidation method with NDIR detection.

■ Sample Preparation

In this study, a commercially available black mass was purchased and prepared as a sample by passing it through a 250 µm sieve (Fig. 1).

Fig. 1 Black Mass Sample

The GB/T 45203-2024 standard requires a processing blank test and two parallel tests for each sample. As shown in Table 1, the measurements in this study included a blank test group (BLK) and two sample test groups (S1 and S2). S1 represents tests conducted on the commercially available black mass. S2 is a contaminated simulated sample to which 0.32 mL of 10,000 mgC/L oxalic acid was added. Additionally, the carbon content of the added oxalic acid was used as a reference for spiked recovery testing.

Table 1 Sample Details for Each Test Group

Sample		Details	Remarks
BLK		Pure water: 80 mL	Blank test
S1	(1)	Black mass: 8.00 g Pure water: 80 mL	Two parallel tests
	(2)		
S2	(1)	Black mass: 8.00 g Pure water: 80 mL Oxalic acid: 10,000 mgC/L, 0.32 mL	Two tests
	(2)		

■ Pretreatment and Analysis with Reference to GB/T 45203-2024

The pretreatment was carried out with reference to the procedures described in GB/T 45203-2024. The pretreatment flow implemented is shown in Fig. 2.

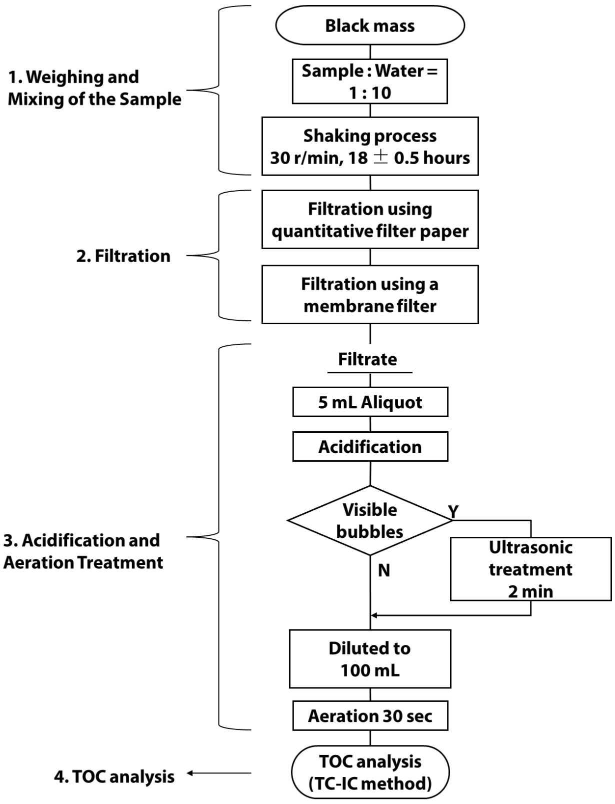


Fig. 2 Pretreatment Flow for Black Mass

1. Weighing and Mixing of the Sample

Black mass weighing 8.00 g was placed into a 160 mL high-density polyethylene (HDPE) container. To achieve a sample-to-water ratio of 1:10, 80 mL of pure water was added.

The sealed container was set on a shaker and subjected to shaking at 30 r/min for 18 ± 0.5 hours.

2. Filtration

After the shaking process, the extract was filtered using 5C quantitative filter paper.

Subsequently, further filtration was performed using a plastic syringe equipped with a polytetrafluoroethylene (PTFE) membrane filter (pore size: 0.22 µm).

3. Acidification and Aeration Treatment

A 5 mL aliquot of the filtrate obtained in the previous step was transferred to a 100 mL volumetric flask. Acidification was carried out using hydrochloric acid (1:1), and the pH of the filtrate was adjusted to below 2.

During the acidification process, visible bubbles were observed forming in the liquid inside the volumetric flask. Therefore, ultrasonic treatment was performed for 2 minutes. The solution was then diluted to 100 mL with pure water.

The prepared solution was subjected to aeration treatment for 30 seconds, followed by TOC analysis.

4. TOC analysis

The GB/T 45203-2024 standard requires TOC analysis using the TC-IC method, where total carbon (TC) and inorganic carbon (IC) are measured separately, and TOC is calculated by subtracting IC from TC.

For the TOC analysis, the Shimadzu TOC-L, a total organic carbon analyzer which utilizes the combustion oxidation method with NDIR detection, as shown in Fig. 3, was used. The measurement conditions are provided in Table 2.

Fig. 3 TOC-L Total Organic Carbon Analyzer (Right)
and ASI-L Auto-Sampler (Left)

Table 2 Measurement Conditions (TC-IC method)

Instrument	TOC-L$_{CPH}$
Catalyst	TOC standard catalyst
Measurement Items	TOC (TC-IC method)
Options	ASI-L auto-sampler
Calibration Curves	TC: 7-point calibration curve using potassium hydrogen phthalate aqueous solutions at 0, 4, 10, 20, 40, 80, and 200 mgC/L
	IC: 7-point calibration curve using sodium bicarbonate and sodium carbonate aqueous solutions at 0, 2, 5, 10, 20, 40, and 100 mgC/L

■ TOC Analysis Using the NPOC Method

In the NPOC method, the sample is acidified by adding acid, and IC is removed through aeration treatment. The measurement is then performed under the assumption that “TC = TOC.” In the NPOC method, the instrument automatically performed acidification and aeration. This method is expected to reduce measurement time compared to the TC-IC method, and only a single calibration curve is required.

Fig. 4 illustrates the pretreatment flow when using the NPOC method. Here, IC in the solution can be efficiently removed through automatic acidification and aeration by the instrument. As a result, Step 3, “Acidification and Aeration Treatment,” in the pretreatment procedure can be omitted. A 5 mL aliquot of the filtrate obtained in Step 2, “Filtration,” was directly diluted to 100 mL in a volumetric flask, and the resulting solution was used as the measurement solution.

When no acidification is performed during pretreatment, the measurement solution becomes alkaline. Therefore, in the NPOC measurement, the acid addition rate was set to a relatively high value of 2.5 %.

The NPOC method is not described in GB/T 45203-2024; however, it is expected to improve processing efficiency by simplifying manual procedures.

The measurement conditions are shown in Table 3.

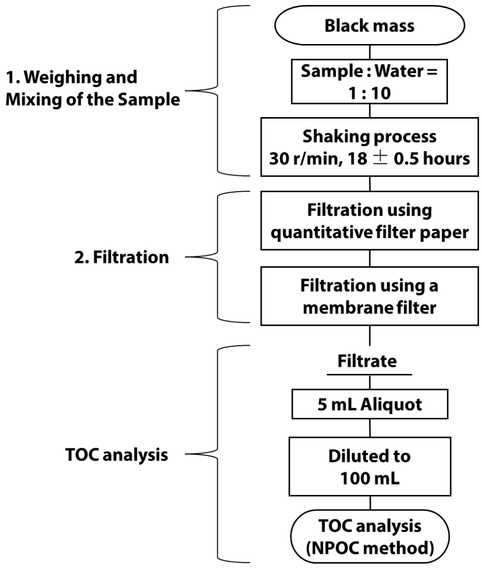


Fig. 4 Pretreatment Flow Using the NPOC Method

Table 3 Measurement Conditions (NPOC method)

Instrument	TOC-L$_{CPH}$
Catalyst	TOC standard catalyst
Measurement Items	TOC (NPOC method)
NPOC Method	Acid addition: 1 mol/L hydrochloric acid, 2.5 %
	Aeration treatment: 80 mL/min, 90 seconds
Options	ASI-L auto-sampler
Calibration Curves	NPOC: 7-point calibration curve using potassium hydrogen phthalate aqueous solutions at 0, 2, 5, 10, 20, 40, and 100 mgC/L

Calibration Curves

The TC calibration curve, created using 7 points of potassium hydrogen phthalate aqueous solutions at 0, 4, 10, 20, 40, 80, and 200 mgC/L, is shown in Fig. 5.

The IC calibration curve, created using 7 points of sodium bicarbonate and sodium carbonate aqueous solutions at 0, 2, 5, 10, 20, 40, and 100 mgC/L, is shown in Fig. 6.

In both cases, the correlation coefficient (r) was 0.9999, indicating excellent linearity.

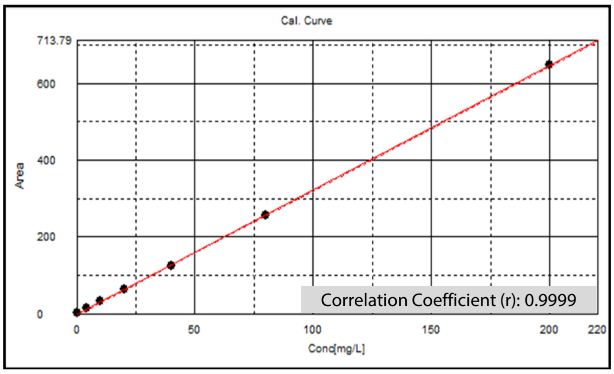


Fig. 5 TC Calibration Curve

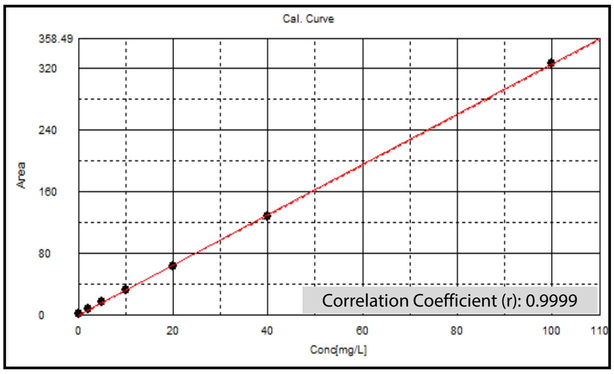


Fig. 6 IC Calibration Curve

The NPOC calibration curve, created using 7 potassium hydrogen phthalate aqueous solutions at 0, 2, 5, 10, 20, 40, and 100 mgC/L, is shown in Fig. 7.

The correlation coefficient (r) was 1.0000, confirming excellent linearity.

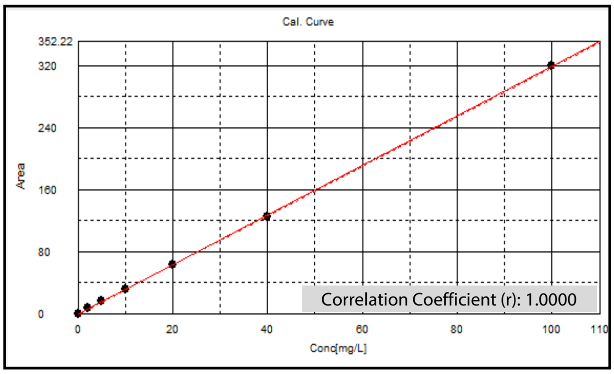


Fig. 7 NPOC Calibration Curve

Measurement Results

The measurement results of the test solutions obtained from each test group (BLK, S1, and S2) using the TC-IC method and the NPOC method are shown in Table 4. Additionally, examples of the measurement data are presented in Figs. 8 to 13.

In the BLK group, it was confirmed that the carbon content derived from pretreatment was minimal. Using the standard catalyst, the limit of quantification (LOQ) of the TOC-L is approximately 0.2 mgC/L for both TC and IC.

For the S1 and S2 test groups, the measurement results obtained using both the TC-IC method and the NPOC method were nearly identical.

In the S2 test group, 0.32 mL of 10,000 mgC/L oxalic acid was added to the initial extract during pretreatment, theoretically increasing the carbon content by 2 mgC/L compared to the S1 test group. As shown in Table 4, the TC-IC method achieved a spiked recovery rate of 97.6 %, while the NPOC method achieved a spiked recovery rate of 99.9 %. This confirms that both methods provide accurate measurements.

Table 4 Measurement Results

Sample		TC-IC method			NPOC method
		TC [mgC/L]	IC [mgC/L]	TOC [mgC/L]	TOC [mgC/L]
BLK		0.09850[*1]	0.03786[*1]	0.06064	0.07750[*1]
S1	(1)	2.515	2.272	0.2431	0.3056
	(2)	1.785	1.570	0.2151	0.2986
	Average Value			0.2291	0.3021
S2	(1)	3.830	1.669	2.161	2.319
	(2)	3.738	1.535	2.203	2.280
	Average Value			2.182	2.300
Spiked Recovery Rate [%] [*2]				97.6	99.9

*1 Below the quantification limit
Under the conditions for the standard catalyst, the limit of quantification for TC and IC is approximately 0.2 mgC/L.

*2 Spiked Recovery Rate [%] = (Average Value of S2 – Average Value of S1) / 2 × 100

Water-Extractable TOC Content in Black Mass

The water-extractable TOC content in black mass was calculated using the following formula. The calculated TOC content values are shown in Table 5.

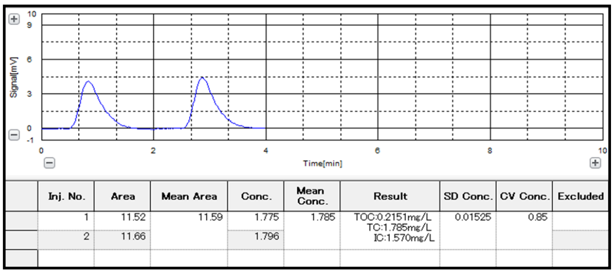
According to the standard, the evaluation criterion for water-extractable TOC content in black mass is 0.10 % or less. It was confirmed that the commercially available black mass (S1) used in this analysis met this criterion.

$$\omega\mathrm{TOC} = \frac{(Ps - Pb) \times V1 \times V2 \times 10^{-6}}{m \times V3} \times 100\ \%$$

ωTOC: Mass fraction of water-extractable TOC
Ps: Average TOC value of the test group (mgC/L)
Pb: TOC value of the blank group (mgC/L)
V1: Volume of pure water used for the extract (mL)
V2: Total volumetric capacity (mL)
V3: Aliquot volume of the filtrate (mL)
m: Weighed sample mass (g)

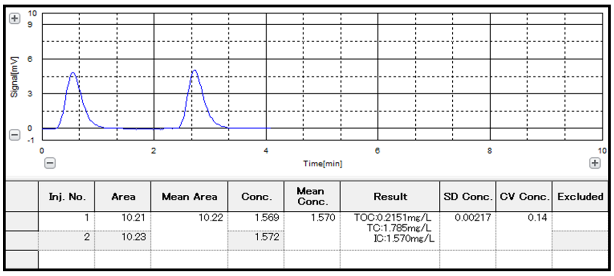
Table 5 Water-Extractable TOC Content in Black Mass

Sample	Water-Extractable TOC Content in Black Mass [wt%]	
	TC-IC method	NPOC method
S1	0.0034	0.0045
S2	0.0424	0.0444



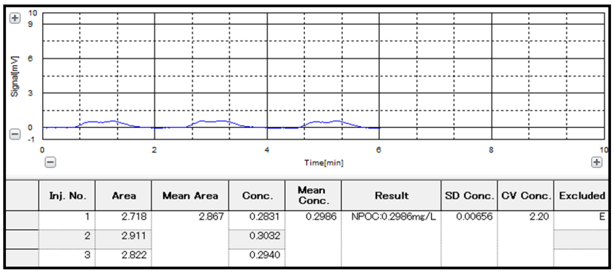
Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
1	11.52	11.59	1.775	1.785	TOC:0.2151mg/L TC:1.785mg/L IC:1.570mg/L	0.01525	0.85	
2	11.66		1.796					

Fig. 8 S1 TC Measurement Data



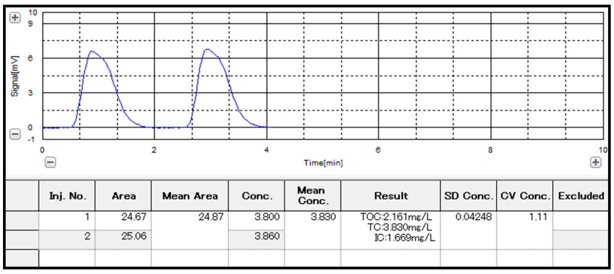
Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
1	10.21	10.22	1.569	1.570	TOC:0.2151mg/L TC:1.785mg/L IC:1.570mg/L	0.00217	0.14	
2	10.23		1.572					

Fig. 9 S1 IC Measurement Data



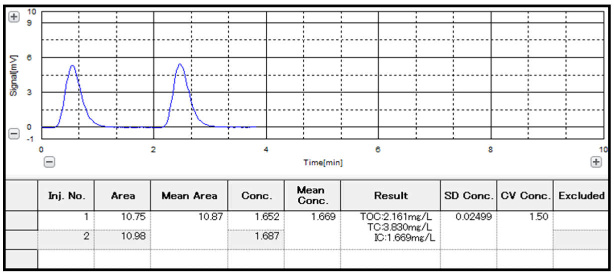
Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
1	2.718	2.867	0.2831	0.2986	NPOC:0.2986mg/L	0.00656	2.20	E
2	2.911		0.3032					
3	2.822		0.2940					

Fig. 10 S1 NPOC Measurement Data



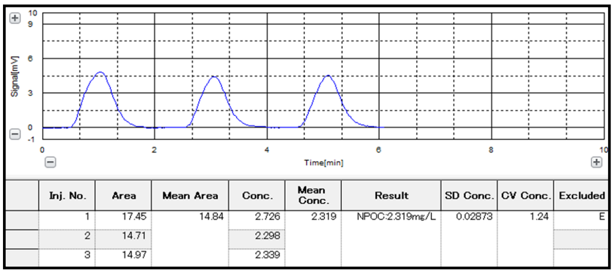
Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
1	24.67	24.87	3.800	3.830	TOC:2.161mg/L TC:3.830mg/L IC:1.669mg/L	0.04248	1.11	
2	25.06		3.860					

Fig. 11 S2 TC Measurement Data



Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
1	10.75	10.87	1.652	1.669	TOC:2.161mg/L TC:3.830mg/L IC:1.669mg/L	0.02499	1.50	
2	10.98		1.687					

Fig. 12 S2 IC Measurement Data



Inj. No.	Area	Mean Area	Conc.	Mean Conc.	Result	SD Conc.	CV Conc.	Excluded
1	17.45	14.84	2.726	2.319	NPOC:2.319mg/L	0.02873	1.24	E
2	14.71		2.298					
3	14.97		2.339					

Fig. 13 S2 NPOC Measurement Data

■ Conclusion

In this study, the water-extractable TOC in recycled black mass was determined using the Shimadzu TOC-L total organic carbon analyzer that uses the combustion oxidation method with NDIR detection.

Pretreatment was performed with reference to GB/T 45203-2024, and it was confirmed that the water-extractable TOC in black mass could be measured using the TC-IC method.

On the other hand, by using the NPOC method, certain pretreatment steps could be omitted, enabling a more simplified quantification of TOC. This method is effective for improving measurement efficiency in applications such as screening.

In both measurement methods, satisfactory results were obtained in the spiked recovery tests, confirming the validity of the analysis. Furthermore, by utilizing the ASI-L auto-sampler, multiple samples can be measured automatically, contributing to improved analytical efficiency.

<Reference>

1) GB/T 45203-2024: Recycled Black Mass for Lithium-Ion Battery

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01-00919-EN First Edition: Sep. 2025

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