

Application News

Total Organic Carbon Analyzer

TOC Evaluation of Surfactants

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User Benefits

- ◆ TOC can be evaluated accurately using the TC-IC method, even for foaming surfactants.
- ◆ The ASI-L autosampler enables automatic, continuous measurement of multiple samples, improving analytical efficiency.

■ Introduction

Surfactants are important chemicals widely used in detergents and dispersants for pharmaceutical equipment cleaning processes, chemical manufacturing processes, and environmental water management. If surfactant residues remain after such processes, they can not only affect manufacturing processes and final product quality, but also increase the organic load in wastewater and environmental water. Therefore, quality control is also needed for organic matter derived from surfactants.

Total organic carbon (TOC) analysis is effective for evaluating the quality of surfactants. In general, the NPOC (non-purgeable organic carbon) method is often selected for TOC measurement in terms of sample volume and analysis time requirements. On the other hand, because surfactants have both hydrophilic and hydrophobic groups in their structure, they tend to foam even at low concentrations. When such samples are measured by the NPOC method, which involves acid addition and sparging, foaming can cause the sample to overflow from the syringe vessel inside the instrument into the waste line. That can result in measurement values that are lower than the true value.

This article compares TOC measurement results for surfactants obtained by the NPOC method and the TC-IC method using the Shimadzu TOC-L total organic carbon analyzer, which uses the combustion oxidation method.

■ Samples and Analysis Conditions

Four sodium dodecylbenzenesulfonate solutions were prepared as surfactant samples, at TOC concentrations of 0.5, 1, 2, and 3 mg/L, respectively (Table 1). TOC measurements of these samples were conducted under the conditions indicated in Table 2. The following two measurement methods were used.

- (1) TC-IC method: TC (total carbon) and IC (inorganic carbon) are measured separately, and then TOC is calculated as their difference ($\text{TOC} = \text{TC} - \text{IC}$).
- (2) NPOC method: TOC is measured as non-purgeable organic carbon (NPOC). After acidifying the sample to a pH < 3, IC is subsequently removed by sparging and the remaining carbon is measured as TC, which is regarded as TOC. The acidification and sparging steps are performed automatically by the instrument.

Table 1 Samples

Sample	Added Carbon Concentration (mg/L) in Sodium Dodecylbenzenesulfonate
1	0.5
2	1
3	2
4	3

Table 2 TOC Analysis Conditions

Instrument:	TOC-L total organic carbon analyzer
Oxidation Method:	680 °C combustion catalytic oxidation
Catalyst:	High sensitivity catalyst
Measurement Items:	NPOC (TOC by acidification and sparging) TOC (TOC by the TC-IC method)
Calibration Curves:	NPOC and TC: 2-point calibration curves based on potassium hydrogen phthalate aqueous solutions at 0 and 5 mgC/L IC: 2-point calibration curve based on sodium bicarbonate/sodium carbonate aqueous solutions at 0 and 5 mgC/L
Injection Volume:	200 µL
Sample:	Commercial sodium dodecylbenzenesulfonate reagent was dissolved in pure water

■ Calibration Curves

The TOC analyzer was calibrated using 2-point calibration curves for potassium hydrogen phthalate at 0 and 5 mgC/L and 2-point calibration curves for sodium bicarbonate/sodium carbonate aqueous solutions at 0 and 5 mgC/L. The potassium hydrogen phthalate calibration curve was used for NPOC and TC measurements and the sodium bicarbonate/sodium carbonate calibration curve was used for IC measurement.

The calibration curves are shown in Figs. 1 (a) to (c).

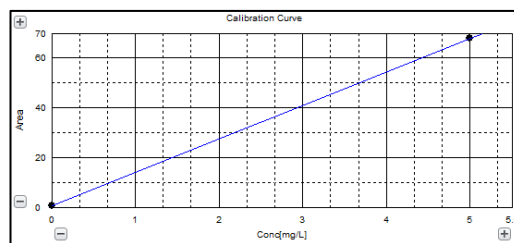


Fig. 1 (a) Calibration Curve Data (NPOC Measurement)

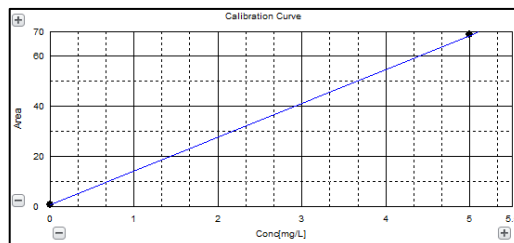


Fig. 1 (b) Calibration Curve Data (TC Measurement)

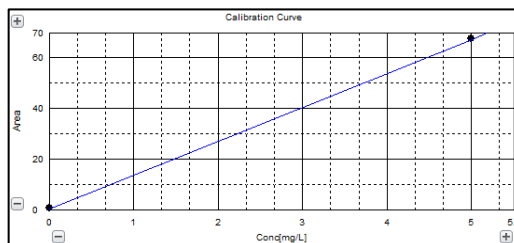


Fig. 1 (c) Calibration Curve Data (IC Measurement)

■ Measurement Results

1. TOC Measurement by the NPOC Method

Table 3 indicates the results obtained when the sodium dodecylbenzenesulfonate solutions were measured by the NPOC method. The TOC recovery rates were below 50 % for all samples. The measurement data for each sample are indicated in Figs. 2 (a) to (d).

Table 3 Summary of Measurement Results by the NPOC Method

Sample	NPOC conc. (mg/L)	Recovery (%)
1	0.2114	42.3
2	0.4796	48.0
3	0.8688	43.4
4	1.386	46.2

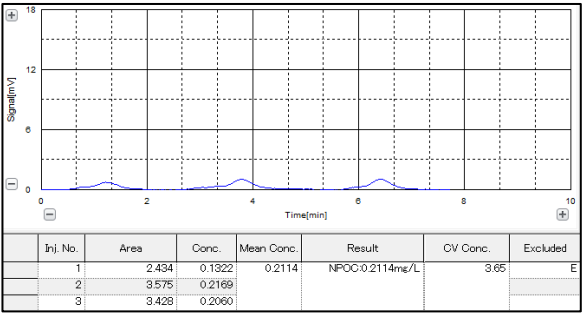


Fig. 2 (a) Sample 1 (0.5 mgC/L, NPOC Measurement)

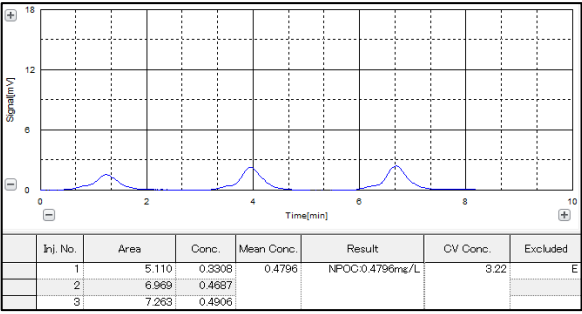


Fig. 2 (b) Sample 2 (1 mgC/L, NPOC Measurement)

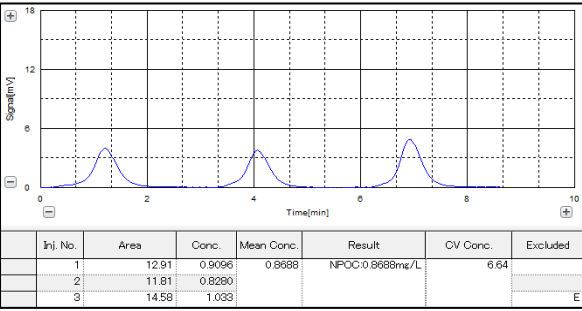


Fig. 2 (c) Sample 3 (2 mgC/L, NPOC Measurement)

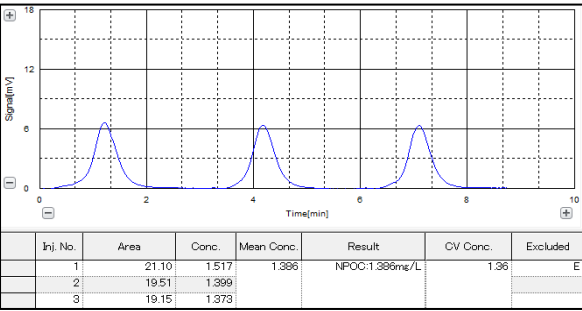


Fig. 2 (d) Sample 4 (3 mgC/L, NPOC Measurement)

2. TOC Measurement by the TC-IC Method

Table 4 shows the results obtained when the sodium dodecylbenzenesulfonate solutions were measured by the TC-IC method. The TOC recovery rates close to 100 % were obtained for all samples. The measurement data for each sample are shown in Figs. 3 (a) to (h).

Table 4 Summary of Measurement Results by the TC-IC Method

Sample	TC conc. (mg/L)	IC conc. (mg/L)	TOC conc. (mg/L)	Recovery (%)
1	0.5127	0.01482	0.4979	99.6
2	1.022	0.02819	0.9941	99.4
3	2.073	0.06437	2.008	100.4
4	3.062	0.02981	3.033	101.1

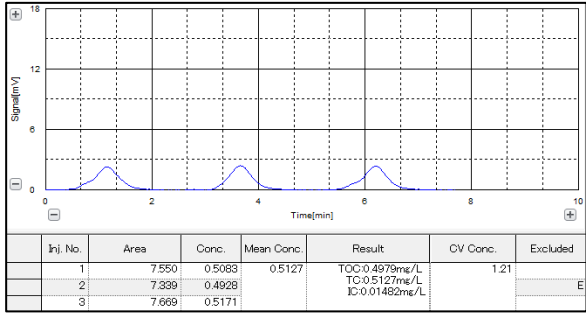


Fig. 3 (a) Sample 1 (0.5 mgC/L, TC Measurement)

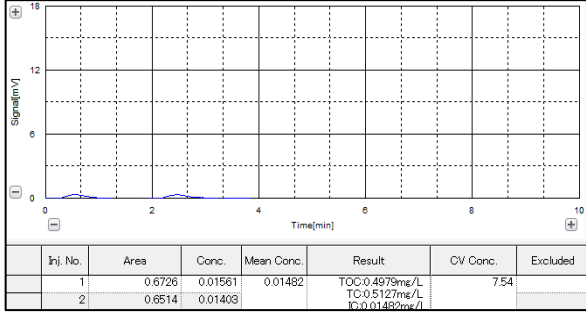


Fig. 3 (b) Sample 1 (0.5 mgC/L, IC Measurement)

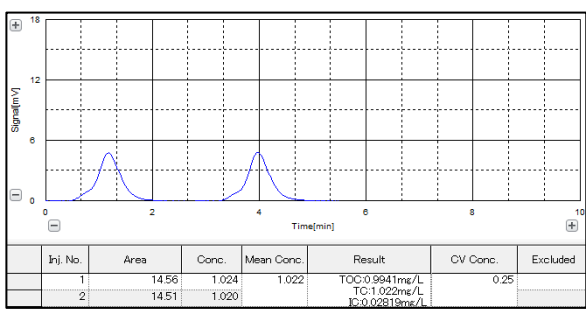


Fig. 3 (c) Sample 2 (1 mgC/L, TC Measurement)

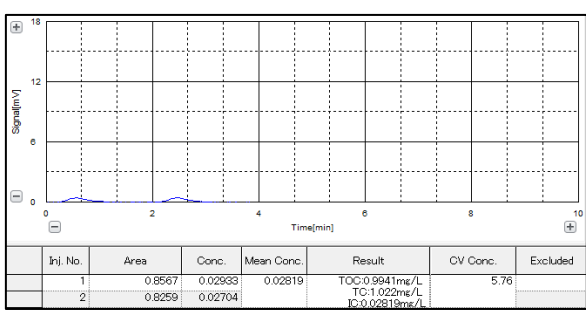


Fig. 3 (d) Sample 2 (1 mgC/L, IC Measurement)

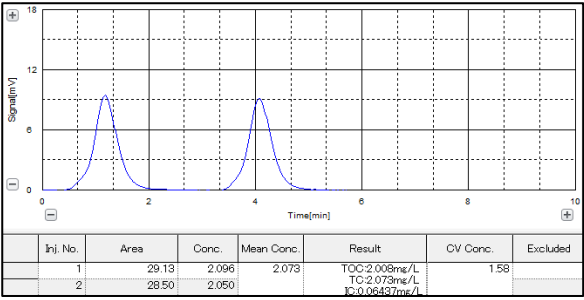


Fig. 3 (e) Sample 3 (2 mgC/L, TC Measurement)

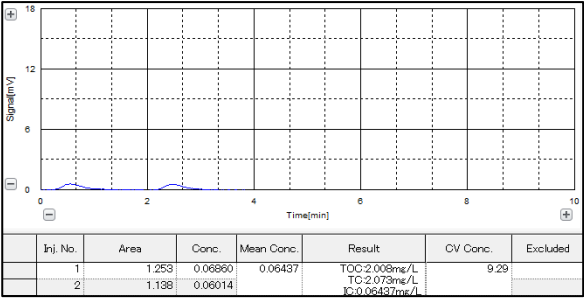


Fig. 3 (f) Sample 3 (2 mgC/L, IC Measurement)

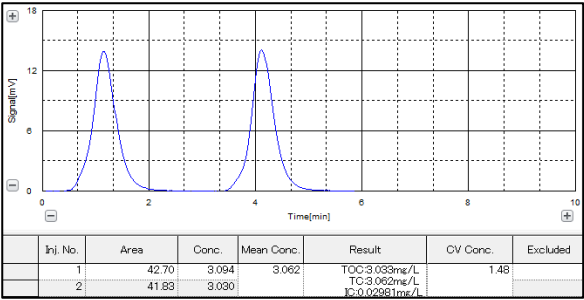


Fig. 3 (g) Sample 4 (3 mgC/L, TC Measurement)

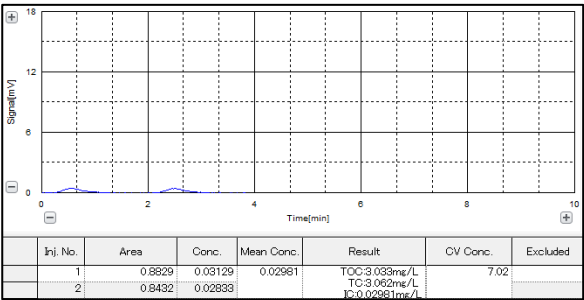


Fig. 3 (h) Sample 4 (3 mgC/L, IC Measurement)

■ Conclusion

Table 5 summarizes the results obtained by measuring sodium dodecylbenzenesulfonate solutions, used here as representative surfactant samples, by the NPOC method and the TC-IC method. With the NPOC method, the TOC recovery rates were below 50 % for all samples, whereas the TC-IC method produced satisfactory TOC recovery rates close to 100 % for all samples.

Table 5 Summary of Measurement Results

Carbon conc. in sample	NPOC method		TC-IC method	
	Conc. (mg/L)	Recovery (%)	Conc. (mg/L)	Recovery (%)
0.5 mg/L	0.2114	42.3	0.4979	99.6
1 mg/L	0.4796	48.0	0.9941	99.4
2 mg/L	0.8688	43.4	2.008	100.4
3 mg/L	1.386	46.2	3.033	101.1

Sodium dodecylbenzenesulfonate solutions (carbon concentration: 0.5 mg/L) is also used in Japanese Pharmacopoeia (JP) recovery tests. For surfactants that readily foam, such as in this example, NPOC measurements involving acid addition and sparging may affect measurement accuracy due to sample loss. For such samples, accurate TOC values can be obtained by using the TC-IC method. In addition, by using the ASI-L autosampler, multiple samples can be measured automatically and continuously.

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