

Application News

Total Organic Carbon Analyzer TOC-L, On-line TOC Analyzer TOC-4200

Detection of Antifreeze (Brine) Leakage into Wastewater

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User Benefits

- ◆ Antifreeze that has leaked into wastewater can be detected with a TOC analyzer with high sensitivity from low concentrations to high concentrations.
- ◆ The on-line TOC analyzer (TOC-4200) can continuously measure samples with a cycle of 10 minutes or less, enabling continuous monitoring of wastewater.
- ◆ The laboratory TOC analyzer (TOC-L) makes it possible to respond to a wide range of applications with a single instrument, including not only wastewater management, but also quality control and investigation and research.

■ Introduction

Ethylene glycol and propylene glycol are used as heat transfer media in air conditioners, refrigerator freezers, and similar equipment. They are also widely used in antifreeze (brine) owing to their low freezing point and low cost. However, ethylene glycol is especially toxic if it is ingested and metabolized in the human body, and causes kidney damage and other health problems. For this reason, it is important to monitor wastewater to enable detection of leakage of antifreeze, and especially contamination of rainwater lines that are not subject to wastewater treatment.

UV analyzers are widely used to monitor organic substances in wastewater, as they are inexpensive and the burden of maintenance is small. However, UV analyzers are not suitable for applications that involve detection of antifreeze leaks because they cannot detect antifreeze agents. On the other hand, because total organic carbon (TOC) analyzers can detect organic compounds regardless of the type, they can reliably detect leaked antifreeze.

Many public regulations on the concentrations of organic compounds in wastewater discharged after water treatment are specified by COD (chemical oxygen demand), and there are also cases where COD analyzers are used in antifreeze leakage detection applications. However, in recent years there has been an ongoing changeover to TOC analyzers in view of the disadvantages of COD measurement, such as the long measurement time and the influence of inorganic salts in samples on measured values.

This article introduces an example of detection of leaked ethylene glycol in wastewater utilizing a Shimadzu TOC-L total organic carbon analyzer, which uses the combustion catalytic oxidation method. In addition, confirmation of the correlation of TOC and COD was conducted.

■ Analysis Method

Six measurement samples (① to ⑥), as shown in Table 1, were prepared by adding wastewater from one of this company's facilities with ethylene glycol so as to obtain carbon concentrations of 1, 5, 10, 20, and 50 mgC/L (carbon concentration in mg/L), and TOC measurements of these samples were conducted under the conditions in Table 2.

Table 1 Measurement Samples

Sample	Added carbon concentration (mgC/L) Ethylene glycol
Sample ①	0
Sample ②	1
Sample ③	5
Sample ④	10
Sample ⑤	20
Sample ⑥	50

Table 2 Measurement Conditions

Analyzer	: TOC-L total organic carbon analyzer
Oxidation method	: 680 °C combustion catalytic oxidation
Catalyst	: Standard catalyst
Measurement item	: NPOC (non-purgeable organic carbon; TOC by acidification and sparging)
Calibration curve	: 2-point calibration curve using 0 to 60 mg/L potassium hydrogen phthalate (aq.)
Injection amount	: 50 µL
Sample	: Wastewater from Shimadzu facility
TOC dopant	: Ethylene glycol (special grade)

■ Measurement Results

Table 3 shows the results of measurements of the wastewater (not added) and samples prepared by adding the wastewater with ethylene glycol. Satisfactory results close to 100 % were obtained for the TOC recovery rates of all samples. Fig. 1 shows the correlation graph of the added concentration and the measured concentration. A good correlation can be confirmed, as the coefficient of correlation is 0.9999. Fig. 2 shows the calibration curve data of the measurements, and Fig. 3 shows the measurement data for each sample.

As demonstrated here, the TOC-L can detect ethylene glycol that has leaked into wastewater over a wide range, from low concentrations to high concentrations.

The measurement described above introduced an analysis example using the TOC-L. However, the TOC-4200, which enables on-line measurement, is an effective instrument for continuously monitoring wastewater. While there are some differences between the TOC-L and the TOC-4200 in terms of whether sample preparation equipment is required or not, the same components are used in many parts, and the principle of measurement is also the same. Results of the same quality as the data obtained with the TOC-L in this measurement can also be obtained with the TOC-4200.

Table 3 Summary of Measurement Results

Sample	TOC measurement value (mgC/L)	TOC recovery rate (%)
Sample ① (additive-free wastewater)	1.09	-
Sample ② (wastewater + 1 mgC/L)	2.08	99.2
Sample ③ (wastewater + 5 mgC/L)	6.10	100.2
Sample ④ (wastewater + 10 mgC/L)	10.8	97.0
Sample ⑤ (wastewater + 20 mgC/L)	20.9	99.1
Sample ⑥ (wastewater + 50 mgC/L)	49.7	97.1

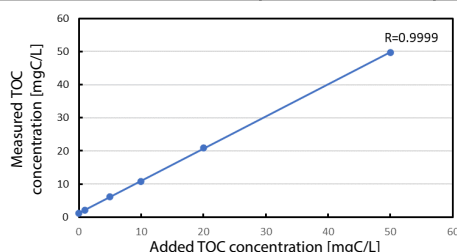


Fig. 1 Correlation Graph of Added Concentration and Measured Concentration

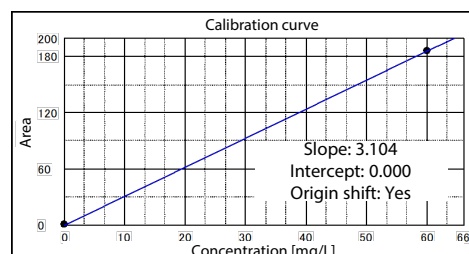
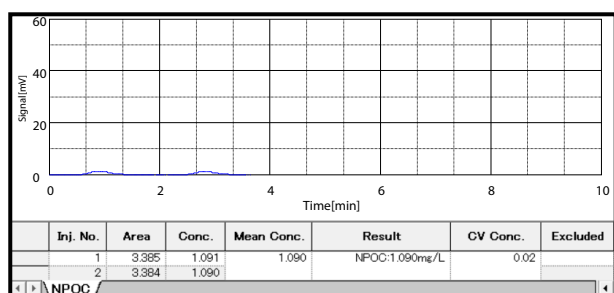
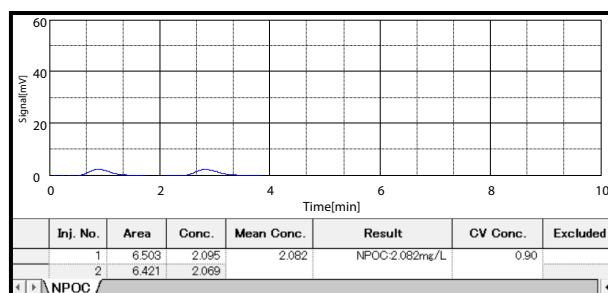


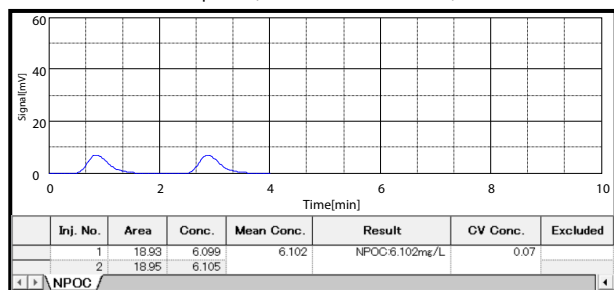
Fig. 2 Calibration Curve Data



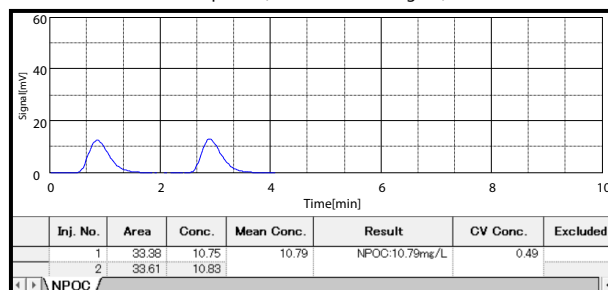
Sample ① (additive-free wastewater)



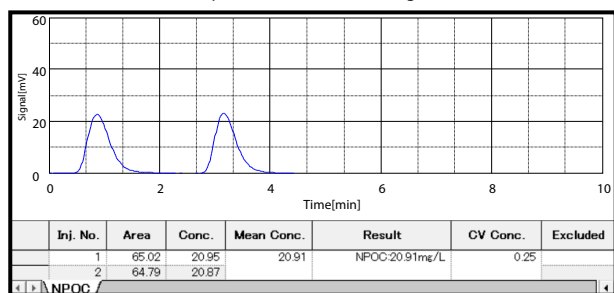
Sample ② (wastewater + 1 mgC/L)



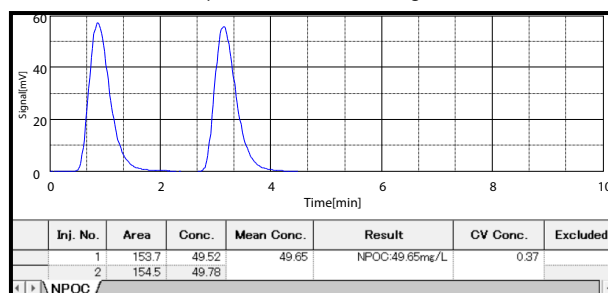
Sample ③ (wastewater + 5 mgC/L)



Sample ④ (wastewater + 10 mgC/L)



Sample ⑤ (wastewater + 20 mgC/L)



Sample ⑥ (wastewater + 50 mgC/L)

Fig. 3 Measurement Data

■ Confirmation of Correlation of TOC and COD

In order to use TOC in management of discharged wastewater, confirmation of the correlation of TOC and COD in the flow channel to be managed may be required. In such cases, it is necessary to confirm the correlation for each flow channel, since it may not be possible to obtain a correlation, depending on the properties of the wastewater.

Therefore, the TOC and COD of the samples in Table 1 were measured and their correlation was confirmed. The COD measurements are carried out by an external organization by the method specified in JIS K 0102 17 Chemical oxygen demand (COD). Table 4 shows a summary of the measurement results, and Fig. 4 shows the correlation graph of TOC and COD.

The coefficient of correlation of TOC and COD was 0.9995 (Fig. 4), indicating that a good correlation was obtained. Based on this result, it is amply possible to detect leaks of antifreeze by TOC, at the same level as with COD.

Table 4 Summary of Measurement Results

Sample	TOC measurement value (mgC/L)	COD measurement value (mgO/L)
Sample ① (additive-free wastewater)	1.09	2.3
Sample ② (wastewater + 1 mgC/L)	2.08	3.0
Sample ③ (wastewater + 5 mgC/L)	6.10	13
Sample ④ (wastewater + 10 mgC/L)	10.8	24
Sample ⑤ (wastewater + 20 mgC/L)	20.9	55
Sample ⑥ (wastewater + 50 mgC/L)	49.7	130

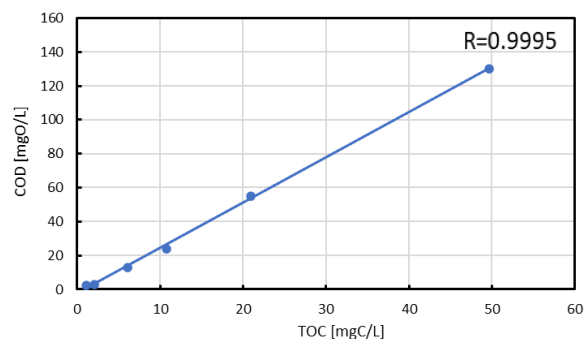


Fig. 4 Correlation Graph of TOC and COD

■ Conclusion

Shimadzu TOC analyzers are capable of detecting antifreeze that has leaked into wastewater over a wide range, from low concentrations to high concentrations.

In addition, the TOC-4200 on-line TOC analyzer makes it possible to measure samples continuously with a cycle of no more than 10 minutes, enabling continuous monitoring of wastewater.

TOC analyzers can measure the total amount of carbon contained in samples and they can also be used in management of all types of organic compounds, not limited to antifreeze. Just one TOC analyzer is sufficient to conduct water quality management with confidence, such as management of wastewater.