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Wet Oxidation Total Organic Carbon Analyzer TOC-V

Application News

Evaluation of TOC of Sulfuric Acid using Wet Oxidation TOC Analyzer

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User Benefits

- It is feasible to quantify low TOC content in 10 % sulfuric acid solution and thereby manage organic contamination within sulfuric acid solutions.
- By using the auto-sampler, multiple samples can be automatically measured.

■ Introduction

Sulfuric acid is one of the chemicals used in the semiconductor industry for precision cleaning of surfaces such as wafers. When the cleaning solution is contaminated with organic impurities, it may not only affect the objects being cleaned but also the manufacturing process itself. Therefore, stringent quality control is imperative for the sulfuric acid utilized in the cleaning process.

Organic impurities in sulfuric acid can be evaluated by measuring total organic carbon (TOC). The wet oxidation TOC analyzer, which is capable of high-sensitivity TOC measurement, is effective for managing trace organic substances required by the increasing complexity of integrated circuits.

This article introduces an example of TOC measurement conducted with the Shimadzu wet oxidation total organic carbon analyzer TOC-V on a 10 % sulfuric acid solution.

■ Sample Preparation

Reagent-grade sulfuric acid was used as the measurement sample in this experiment. The sulfuric acid sample was diluted tenfold with pure water to prepare a 10 % sulfuric acid solution. Additionally, potassium hydrogen phthalate was added to the 10 % sulfuric acid solution to prepare samples with TOC concentrations of 0.1 mgC/L, 0.2 mgC/L, 0.3 mgC/L, and 0.5 mgC/L, respectively, and recovery tests were conducted. Table 1 summarizes the sample preparation.

Table 1 Sample Preparation

Samples	TOC [mgC/L]
10 % sulfuric acid solution	0
10 % sulfuric acid solution + TOC 0.1 mgC/L	0.1
10 % sulfuric acid solution + TOC 0.2 mgC/L	0.2
10 % sulfuric acid solution + TOC 0.3 mgC/L	0.3
10 % sulfuric acid solution + TOC 0.5 mgC/L	0.5

■ Analysis Method

The wet oxidation total organic carbon analyzer TOC-V as depicted in Figure 1 was used for the analysis.

The measurement conditions are detailed in Table 2. The TOC measurement employed the non-purgeable organic carbon (NPOC) method. In the NPOC method, the sample is acidified through acid addition, followed by sparging treatment to remove inorganic carbon (IC), with the Total Carbon (TC) then measured as TOC. In this specific case, since the sulfuric acid solution was already acidic, the acid addition step was omitted and only sparging was performed during IC removal.

Calibration of the instrument was performed using potassium hydrogen phthalate aqueous solutions with concentrations of 0 mgC/L, 0.1 mgC/L, 0.5 mgC/L and 1 mgC/L. To account for the TOC component present in the pure water used in preparing the standard solution, an origin shift was applied to the calibration curve.

Fig. 1 Wet Oxidation Total Organic Carbon Analyzer TOC-V

Table 2 Measurement Conditions

Instrument	Wet Oxidation TOC Analyzer TOC-Vwp
Oxidation Method	Oxidation by oxidant, UV irradiation, and heating
Oxidant	Sodium peroxodisulfate
Measurement Items	NPOC (= TOC using acidification and sparging)
Injection Volume	3000 µL
Calibration Curve	TC: 4-point calibration curve with 0, 0.1, 0.5, 1 mgC/L of potassium hydrogen phthalate aqueous solutions

■ Measurement Results

Table 3 Measurement Results of 10 % Sulfuric Acid Solution

Samples	TOC [mgC/L]	CV [%]	Recovery Rate [%]
10 % sulfuric acid solution	0.0185	1.88	-
10 % sulfuric acid solution + TOC 0.1 mgC/L	0.122	0.27	103
10 % sulfuric acid solution + TOC 0.2 mgC/L	0.219	0.32	100
10 % sulfuric acid solution + TOC 0.3 mgC/L	0.316	0.75	99.3
10 % sulfuric acid solution + TOC 0.5 mgC/L	0.518	1.72	100

Here table 3 shows the results of TOC measurement in the 10 % sulfuric acid solution, including the TOC measured values, the coefficient of variation (CV) and the TOC recovery rates. All samples yielded recovery rates within the range of 99.3 % to 103 %.

Fig. 2 shows the correlation between the added TOC concentrations and the measured TOC concentrations. A strong correlation with a correlation coefficient of 0.9999 was established which suggests that the added TOC was accurately measured.

Detailed peak data are shown in Fig. 3. In all measurements, the coefficient of variation remained below 2 %, indicating excellent repeatability.

The results of this study clearly demonstrate that the wet oxidation TOC-V analyzer can quantitatively measure TOC concentrations in 10 % sulfuric acid solution with a reliable measurement accuracy of approximately 0.1 mgC/L.

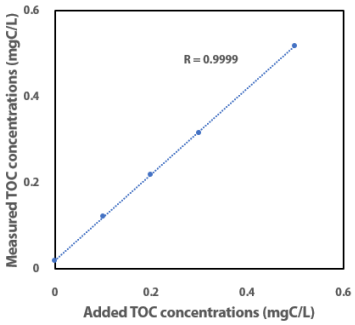
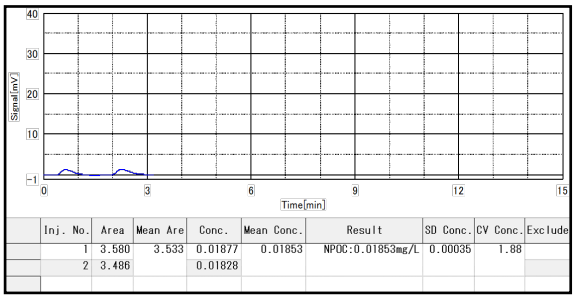


Fig. 2 Correlation between the Added TOC Concentrations and the Measured TOC Concentrations

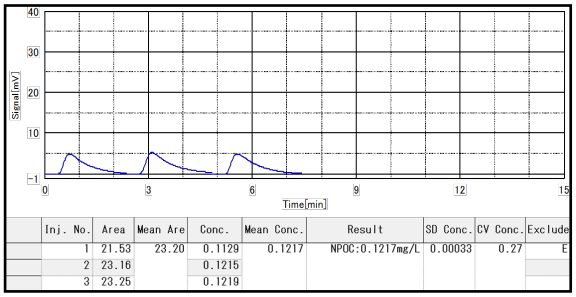
■ Conclusion

The capability to measure low-concentration TOC in 10 % sulfuric acid solution by using the wet oxidation total organic carbon analyzer TOC-V is confirmed. When high-purity sulfuric acid is required, as in industries like semiconductor manufacturing, the use of the wet oxidation TOC-V analyzer can facilitate the management of organic impurities in sulfuric acid, offering the potential for its utilization in quality assessment. Additionally, the use of an autosampler enables the automated measurement of multiple samples, contributing to improved analytical efficiency.

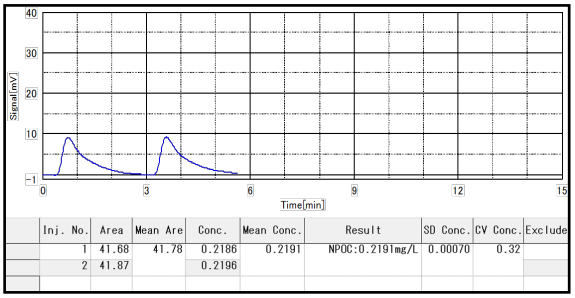
Furthermore, application news 01-00535 introduces the combustion catalytic oxidation TOC-L analyzer, which is used to measure TOC in approximately 1 % sulfuric acid solution.



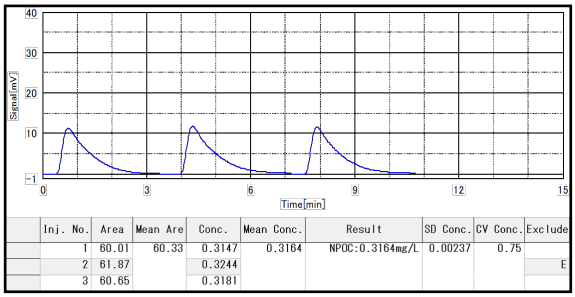
(a) 10 % Sulfuric Acid Solution



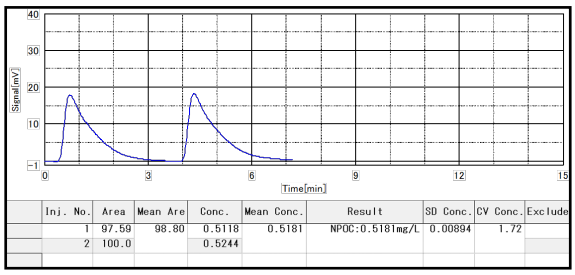
(b) 10 % Sulfuric Acid Solution + TOC 0.1 mgC/L



(c) 10 % Sulfuric Acid Solution + TOC 0.2 mgC/L



(d) 10 % Sulfuric Acid Solution + TOC 0.3 mgC/L



(e) 10 % Sulfuric Acid Solution + TOC 0.5 mgC/L

Fig. 3 Results of TOC Measurements in 10 % Sulfuric Acid Solution

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