

User Benefits

- ◆ It is possible to manage organic contamination in sulfuric acid.
- ◆ By using the ASI-L auto-sampler, multiple samples can be automatically measured.

Introduction

Sulfuric acid is an essential chemical compound with diverse applications, including its use as a fertilizer raw material, in metal refining, and paper production. Ensuring the quality of sulfuric acid is crucial due to the potential impact of impurities on both the manufacturing process and the final products. In industries like semiconductor manufacturing, sulfuric acid is utilized as a cleaning agent. If organic impurities from the cleaning agent remain on the wafer surface, it can not only diminish the quality of the wafer and semiconductor products but also potentially disrupt the entire manufacturing process.

Total organic carbon (TOC) serves as an effective indicator for detecting organic contaminants in sulfuric acid. However, the presence of high concentrations of sulfate ions can influence measurement accuracy. Nevertheless, the Shimadzu TOC-L Total Organic Carbon Analyzer allows direct measurement of sulfuric acid within a concentration range of up to 1 %.

This article provides an example of TOC measurements conducted using the Shimadzu TOC-L analyzer for a 1 % sulfuric acid solution.

Sample Preparation

In this experiment, a 1 % sulfuric acid solution was prepared by diluting reagent-grade sulfuric acid with pure water. To create solutions for the recovery test, potassium hydrogen phthalate was added to the 1 % sulfuric acid solution, resulting in TOC concentrations of 1 mgC/L, 5 mgC/L, and 10 mgC/L, respectively. Table 1 summarizes the sample preparation.

Table 1 Sample Preparation

Samples	TOC [mgC/L]
1 % sulfuric acid solution	0
1 % sulfuric acid solution + TOC 1 mgC/L	1
1 % sulfuric acid solution + TOC 5 mgC/L	5
1 % sulfuric acid solution + TOC 10 mgC/L	10

Analysis Method

The TOC-L Total Organic Carbon Analyzer was employed for the analysis. The measurement conditions are presented in Table 2. The TOC measurement was conducted using the non-purgeable organic carbon (NPOC) method. In the NPOC method, the sample is typically acidified to remove inorganic carbon (IC) by sparging, and the resulting total carbon (TC) is measured as TOC. However, given that sulfuric acid samples are already acidic, no additional acid was introduced, and only sparging was performed for removal of IC.

Calibration of the instrument was performed using potassium hydrogen phthalate aqueous solutions with concentrations of 0 mgC/L and 20 mgC/L for TC measurements. 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 TOC-L Total Organic Carbon Analyzer (right) and ASI-L Auto-Sampler (left)

Table 2 Measurement Conditions

Instrument	TOC-L _{CPH} Total Organic Carbon Analyzer
Catalyst	Standard catalyst
Measurement Items	NPOC (= TOC using acidification and sparging)
Injection Volume	50 µL
Calibration Curves	TC: 2-point calibration curve with 0 and 20 mgC/L of potassium hydrogen phthalate aqueous solution

Measurement Results

Table 3 Measurement Results of 1 % Sulfuric Acid Solution

Samples	TC [mgC/L]	Recovery Rate [%]
1 % sulfuric acid solution	0.343	-
1 % sulfuric acid solution + TOC 1 mgC/L	1.34	99.9
1 % sulfuric acid solution + TOC 5 mgC/L	5.35	100
1 % sulfuric acid solution + TOC 10 mgC/L	10.6	102

The results of measuring TOC in the 1 % sulfuric acid solution are presented in Table 3. All samples had a recovery rate ranging from 99.9 % to 102 %.

Fig. 2 shows the correlation between the added TOC concentration and the measured TOC concentration. The obtained correlation coefficient of 0.9999 indicates a strong correlation, affirming the accurate measurement of the added TOC. Detailed peak data are shown in Fig. 3.

The results demonstrate that using the TOC-L enables the measurement of TOC in 1 % sulfuric acid solution without any interference from sulfate ions, resulting in a reliable measurement accuracy of approximately 1 mgC/L.

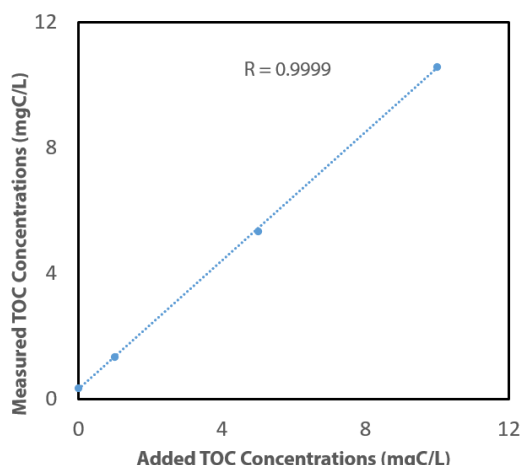


Fig. 2 Correlation between the Added TOC Concentrations and the Measured TOC Concentrations

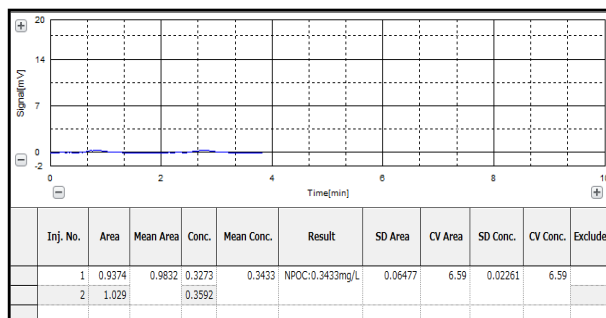
Conclusion

This article has confirmed the suitability of the Shimadzu TOC-L analyzer for TOC analysis of 1 % sulfuric acid solution. For higher concentrations of sulfuric acid, proper dilution is necessary to ensure accurate measurements.

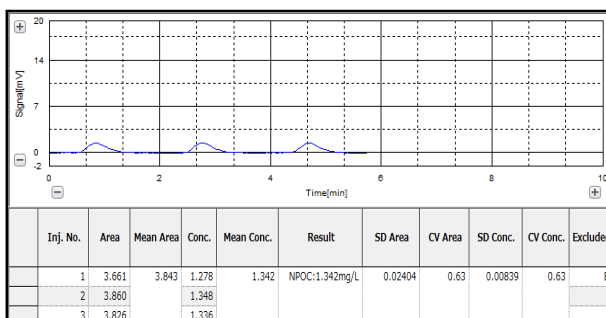
Using the TOC-L provides the means to effectively manage organic impurities in sulfuric acid. This capability is particularly valuable for assessing the quality of organic compounds, especially in industries like semiconductor manufacturing that require high-purity sulfuric acid.

Furthermore, the integration of the ASI-L autosampler facilitates automated measurement of multiple samples, contributing to improved analysis efficiency.

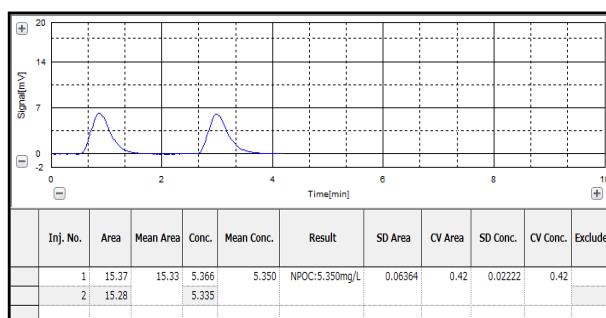
* Please note that in this application news, the maximum sulfuric acid solution concentration that can be measured is 1%.
 * Measurements of TOC at concentration exceeding 1% sulfuric acid solution may not be feasible.



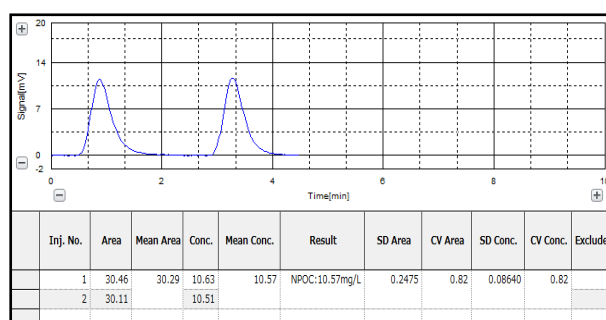
(a) 1 % Sulfuric Acid Solution



(b) 1 % Sulfuric Acid Solution + TOC 1 mgC/L



(c) 1 % Sulfuric Acid Solution + TOC 5 mgC/L



(d) 1 % Sulfuric Acid Solution + TOC 10 mgC/L

Fig. 3 Results of 1 % Sulfuric Acid Solution TOC Measurement



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01-00535-EN

First Edition: Aug. 2023