

Application News

No. AD-0174

TOC-VWP/Sulfuric acid/Semiconductor

Determination of Organic Contaminants in Sulfuric Acid using Wet Oxidation Type Total Organic Carbon Analyzer

□ Introduction

Sulfuric acid (H₂SO₄) is widely used in the semiconductor industry for the manufacturing of integrated circuits to resist stripping and wafer cleaning. Any organic contaminants remaining on the wafer surfaces could have a detrimental effect on the wafers as well as the process equipment [1].

Total Organic Carbon (TOC) can be used to indicate organic contaminants in sulfuric acid. The TOC-L series catalytic combustion system with High Salt Kit has been used to measure TOC in sulfuric acid [2]. To prevent damage by fumes from concentrated 96% sulfuric acid, the sample was diluted 10 times and SO₂ scrubbers were used to protect the instrument. Using this configuration, sulfuric acid with TOC content of less than 10 ppm can be measured.

Due to the more sophisticated integrated circuits, there is an increasing demand in the semiconductor industry for ultra pure sulfuric acid with lesser organic impurities. To analyze low TOC content, a wet oxidation type TOC analyzer can be used as it has better detection limit than catalytic combustion type TOC analyzer. This application news describes the use of wet oxidation type TOC analyzer to measure TOC in sulfuric acid.

□ Experimental

The potassium hydrogen phthalate used to prepare the Total Carbon (TC) standard solutions was from Kanto Chemical Co Ltd, Japan. The sodium persulfate was purchased from Sigma-Aldrich, USA whereas the 85% H₃PO₄ was purchased from Merck, Germany. Ultra pure water (H₂O) used in this analysis was produced by reverse osmosis, electrodeionisation, UV and finally filtered by a 0.22 mm filter to produce H₂O with resistivity of 18 MΩ using the Milli-Q® system from Millipore, Germany.

The sulfuric acid samples (ACS grade, ≥ 95 %) were from JT Baker, USA and an electronic company in Singapore. The sulfuric acid samples were diluted 10 or 20 times prior to analysis.

The 1000 ppm Non-Purgeable Organic Carbon (NPOC) standard solution, Oxidant and Acid reagents were prepared as described in the TOC-VWP User's Manual [3]. The TOC analysis conditions are shown in Table 1.

Table 1: Instrument and Analytical Conditions

Instrument	: TOC-VWP
Detector	: Non-Dispersive Infrared (NDIR)
Method	: NPOC
UV	: 185 and 254 nm
Oxidant	: 1.5 mL
Heater	: 80 °C
Acid	: 1 %
Sparging Time	: 3 minutes
No. of Wash	: 1
Injection Volume	: 3 mL
Scrubber	: Mist scrubber (between dehumidifier and halogen scrubber)
Calibration Curve	: Non-zero shift

□ Results and Discussion

The calibration curve has a coefficient of linear regression (R²) of more than 0.9990 (Figure 1) and good reproducibility as the relative standard deviation (% RSD) was less than 3 % (Table 2).

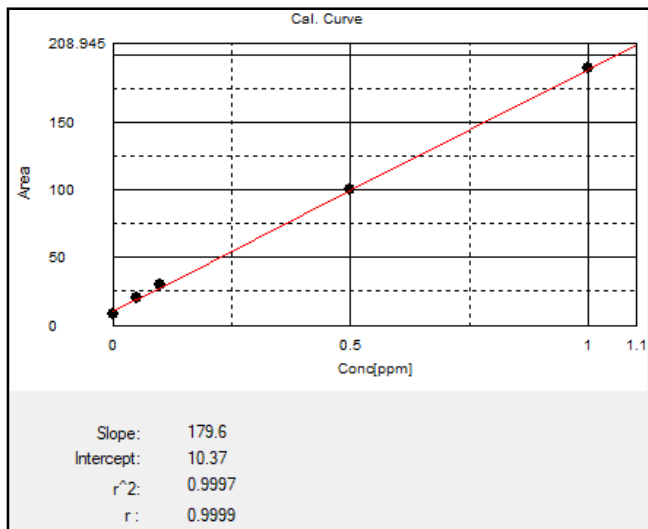


Figure 1: NPOC Calibration Curve

Table 2: NPOC Calibration Curve Results

Standard Concentration	Average Area (2 injections)	% RSD
0.00 ppm	8.41	2.2 %
0.05 ppm	20.50	0.9 %
0.10 ppm	29.46	0.9 %
0.50 ppm	99.92	0.3 %
1.00 ppm	190.00	0.6 %

The limit of detection (LOD) is calculated by dividing the slope of calibration curve by the area which is equal to 3.3 times the standard deviation (SD) of the 10 repetition measurement of the blank solution (ultra-pure water) [4]. The LOD obtained was 0.01 ppm.

The TOC results for sulfuric acid samples are shown in Table 3. The spike recovery results of almost 100 % show that there is no matrix interference when the sulfuric acid samples were diluted 10 or 20 times. It is also possible to measure sulfuric acid samples with TOC of less than 1 ppm.

Table 3: TOC Results in Sulfuric Acid Samples

Sample	Conc. (ppm) / (% RSD)	% Spike Recovery	Actual Conc. (ppm)
Sample-1 diluted 20 X	0.1072 (1.0 %)	-	2.14
Sample-1 diluted 20 X + 0.5 ppm Standard	0.6070 (1.4 %)	100.0 %	-
Sample-2 diluted 10 X	0.0091 (1.1 %)	-	0.09
Sample-2 diluted 10 X + 0.1 ppm Standard	0.1091 (0.8 %)	100.0 %	-
Sample-2 diluted 10 X + 0.2 ppm Standard	0.2109 (0.5 %)	100.9 %	-

Conclusions

Wet oxidation type TOC analyzers can be used to determine TOC in sulfuric acid. To minimise matrix interference, concentrated sulfuric acid samples should be diluted to less than 10 % acid prior to analysis. This method is suitable for semiconductor or other applications that requires sulfuric acid with less than 1 ppm TOC.

References

- Electronic Chemicals No PB1031011Rev10 (2011). Honeywell International Inc.
- Shimadzu Application News SCA-130-303 (2015). TOC – Determination in sulfuric acid.
- Shimadzu TOC-VWP User's Manual (2013).
- TOC-LCPH - TOC Detection Limit Test Standard Operating Procedures (ZEHV-0225).

Milli-Q is a trademark of Merck KGaA, Darmstadt, Germany or its affiliates. Third-party trademarks and trade names may be used in this publication to refer to either the entities or their products/services, whether or not they are used with trademark symbol "TM" or "®".

Copyright © 2018 SHIMADZU (Asia Pacific) Pte. Ltd. All rights reserved. No part of this document may be reproduced in any form or by any means without permission in writing from SHIMADZU (Asia Pacific) Pte. Ltd.