

Application Notes

Total Organic Carbon

Analysis of Organic Impurities in Phosphoric Acid with TOC Analyzer

Introduction

The use of phosphoric acid (H_3PO_4) solutions is common in the semiconductor industry to both clean and etch metal surfaces⁽¹⁾. However, the quality of H_3PO_4 deteriorates if organic matter concentration increases due to impurities and chemicals (surface-active agent, etc), and etching speed also slows down⁽³⁾. Hence, controlling the concentration of organic impurities is important to ensure that the etching process is proceeding smoothly. The organic carbon impurities content can be monitored using a Total Organic Carbon (TOC) analyzer⁽²⁾.

TOC is determined using the equation:

$$\begin{aligned}\text{TOC} &= \text{TC} - \text{IC} \text{ where} \\ \text{TC} &= \text{Total Carbon} \\ \text{IC} &= \text{Inorganic Carbon}\end{aligned}$$

Shimadzu has 2 types of laboratory type TOC analyzers based on the type of method used to measure TC. They are:

- 1) TOC-VC series which uses platinum catalyst and combustion at 680°C .
- 2) TOC-VW series which uses the wet oxidation method comprising of ultra-violet irradiation, heat and persulfate reagents.

It is more suitable to use the wet oxidation method to determine TOC in H_3PO_4 as H_3PO_4 can melt and damage the platinum catalyst used in TOC-VC series. In this article, the determination of TOC in H_3PO_4 by TOC-VWP is shown.

Materials & Methods

The potassium hydrogen phthalate used to prepare the TC standard solutions, sodium hydrogen carbonate and sodium carbonate used in preparation of IC standard solutions were from Kanto Chemical Co Ltd, Japan. The sodium persulfate and 85% H_3PO_4 were purchased from Merck, Germany.

Ultra pure water (H_2O) used in this analysis was produced by reverse osmosis, electrodeionisation, UV and finally filtered by a $0.22\ \mu\text{m}$ filter to produce H_2O with resistivity of $18\ \text{M}\Omega$ using the Milli-Q system from Millipore, USA.

The same 85% H_3PO_4 from Merck, Germany was also used as sample. To reduce the viscosity of 85% H_3PO_4 for easier sampling by the TOC-VWP, it was diluted 2 times with H_2O prior to analysis. The diluted H_3PO_4 was also added (spiked) with TC standard solution to a final concentration of 1 and 2ppm for matrix interference studies.

Results

The peak profiles for H_3PO_4 spiked with TC standard solutions are shown in Figure 1. H_3PO_4 does not have matrix interference in TOC analysis as good recovery could be obtained (Table 1).

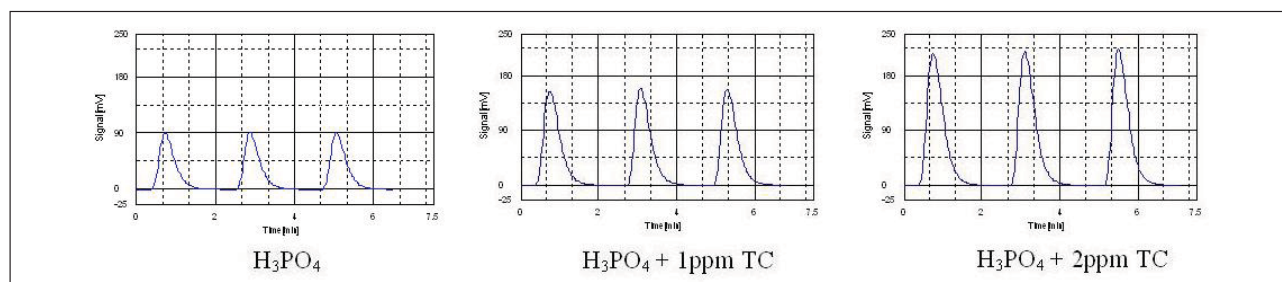


Figure 1. Peak profiles for H_3PO_4 and H_3PO_4 spiked with TC standard solutions.

Sample	Measured TC Concentration	Percentage TC Recovery
H ₃ PO ₄	1.138ppm	-
H ₃ PO ₄ + 1ppm TC	2.134ppm	99.6%
H ₃ PO ₄ + 2ppm TC	3.046ppm	95.4%

Table 1. Matrix interference studies for H₃PO₄.

The TC and IC calibration curves are shown in Figures 2 and 3 whereas the TOC measurement results in H₃PO₄ are summarised in Table 2.

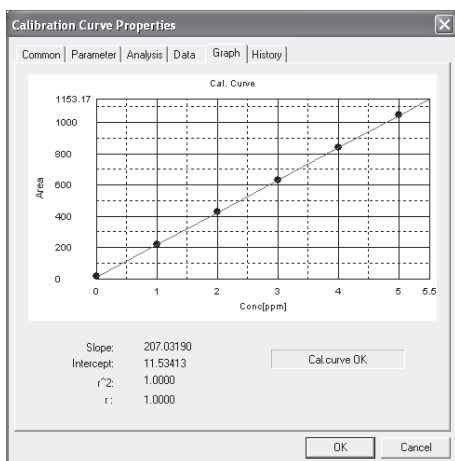


Figure 2. TC calibration curve.

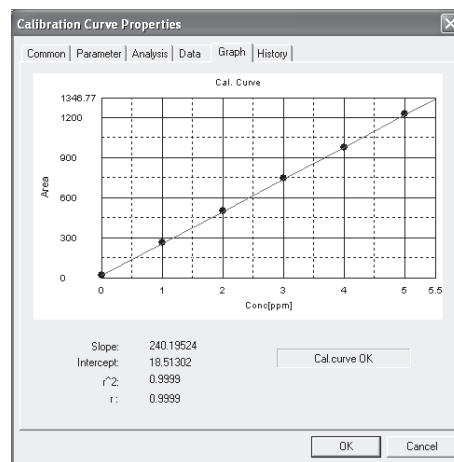


Figure 3. IC calibration curve.

Sample	TC Concentration	IC Concentration	TOC Concentration
H ₃ PO ₄	2.276ppm (RSD = 0.33%)	0.052ppm (RSD = 0.65%)	2.224ppm

Table 2. TOC concentration in H₃PO₄.

Conclusions

The wet oxidation type TOC analyzer can be used to measure organic carbon impurities in H₃PO₄. The Shimadzu TOC-VW series is suitable for this purpose as the results have good repeatability and there is no matrix interference.

References

- (1) Application – phosphoric acid concentration (2005). Guided Wave Incorporated. Literature No. 3006-05-09 Rev A1.
- (2) Measurement of TOC in Electroplating Solution Using TOC-VWS. Shimadzu Application News No 031#LAAN-A-TC-E008.
- (3) TOC measuring of etching solutions for etching process by using the TOC-5000A. Shimadzu TOC.TN Application News No 3.

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