SHIMADZU APPLICATION NEWS

LAAN-A-TC-E008

● TOTAL ORGANIC CARBON ANALYSIS

No.031

Measurement of TOC in Electroplating Solution Using TOC-Vws

Organic additives are added to the electroplating solutions used in copper and nickel plating processes in PCB (Printed Circuit Board) production. The additives affect the plating quality and so controlling their concentrations is important for ensuring the quality of the PCBs. The concentrations of these additives can be controlled using a TOC analyzer.

In general, electroplating solutions contain hydrosulfate at concentrations of a few percent or more. In order to avoid interference, dilution by a factor of at least 100 is required to use a combustion catalytic oxidation TOC analyzer. With a wet oxidation TOC analyzer, however, there is no interference, so other forms of the pretreatment like sample dilution is not required, and organic substances present in low concentrations in the electroplating solution can be measured accurately. Electroplating solutions that contain high concentrations of additive (i.e., 1,000 mgC/L or higher) and that can be greatly diluted can be measured using a combustion catalytic oxidation TOC analyzer. On the other hand, electroplating solutions that contain low concentrations of additive (i.e., 100 mgC/L or lower) and that cannot be greatly diluted can be measured accurately using a wet oxidation TOC analyzer.

In the PCB plating process, the electroplating solution is contaminated by the elution of organic substances from the board material itself. With electroplating solutions that contain low concentrations of additive, however, this organic contamination can be controlled using a TOC analyzer.

In this application news, we present an example of the measurement of copper plating solution performed using Shimadzu Wet oxidation TOC Analyzer TOC-Vws.

■ ①Measurement of TOC in Copper Plating Solution

Fig.1 shows the results obtained by measuring two types of copper plating solution. A calibration curve was created for TC measurement using potassium hydrogen phthalate standard solutions at concentrations of 0 mgC/L and 2 mgC/L and a calibration curve was created for IC measurement using sodium carbonate and sodium hydrogen carbonate standard solutions at concentrations of 0 mgC/L and 1 mgC/L. In order to eliminate the influence of the carbon content in the pure water used to prepare the standard solutions, the calibration curves were corrected by moving to the origin.

The samples were measured without performing dilution or any other form of pretreatment.
(Table 1)

<Measurement Conditions>
Analyzer : Shimadzu Wet oxidation TOC analyzer TOC-Vws
Measurement item : TOC (TC-IC)
Sample : Copper plating solution (copper sulfate: approx. 13%)

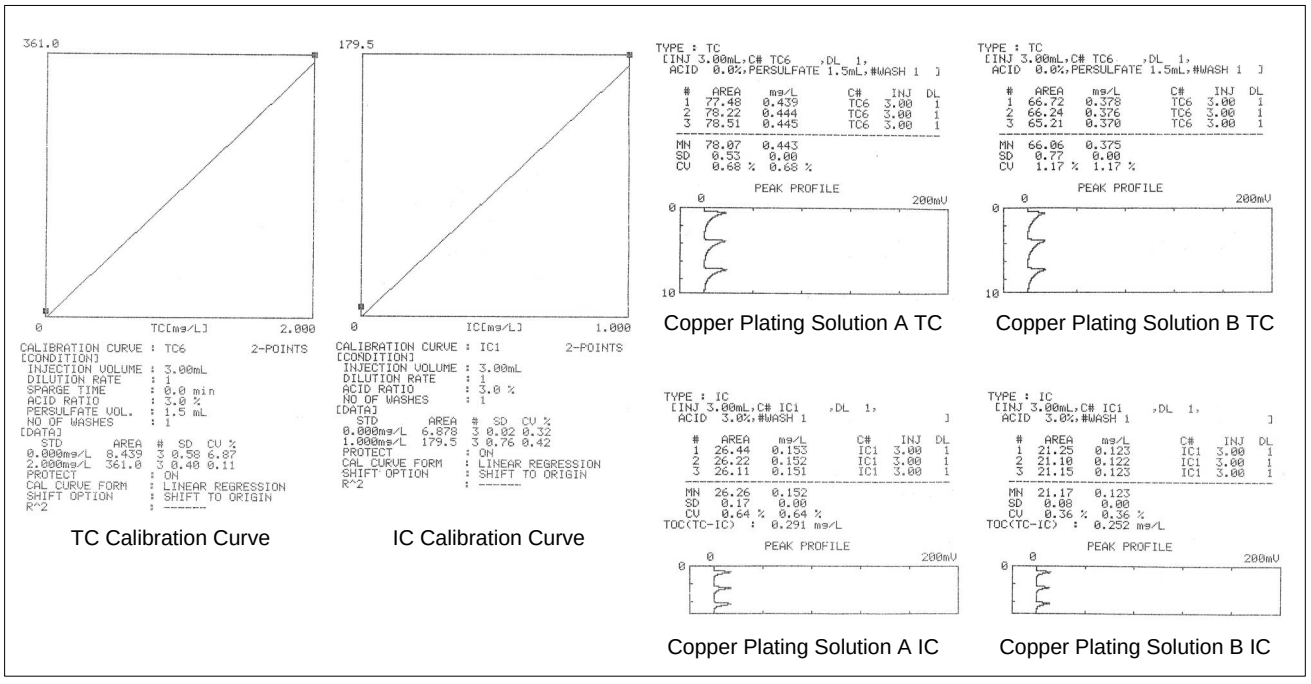


Fig. 1 Measurement of TOC in Electroplating Solution

Table 1 Measurement of TOC in Electroplating Solution

Sample name	TC[mgC/L]	IC[mgC/L]	TOC (TC-IC)[mgC/L]
Copper plating solution A	0.443	0.152	0.291
Copper plating solution B	0.375	0.123	0.252

■ ②Spike Test for TOC in Copper Plating Solution

Potassium hydrogen phthalate was added, as an organic compound, to the two types of copper plating solution that measured in ① to a concentration of 1 mgC/L. The results obtained by performing recovery tests on these recovery solutions are shown in Fig.2. The calibration curves used were the same as those used in ①.

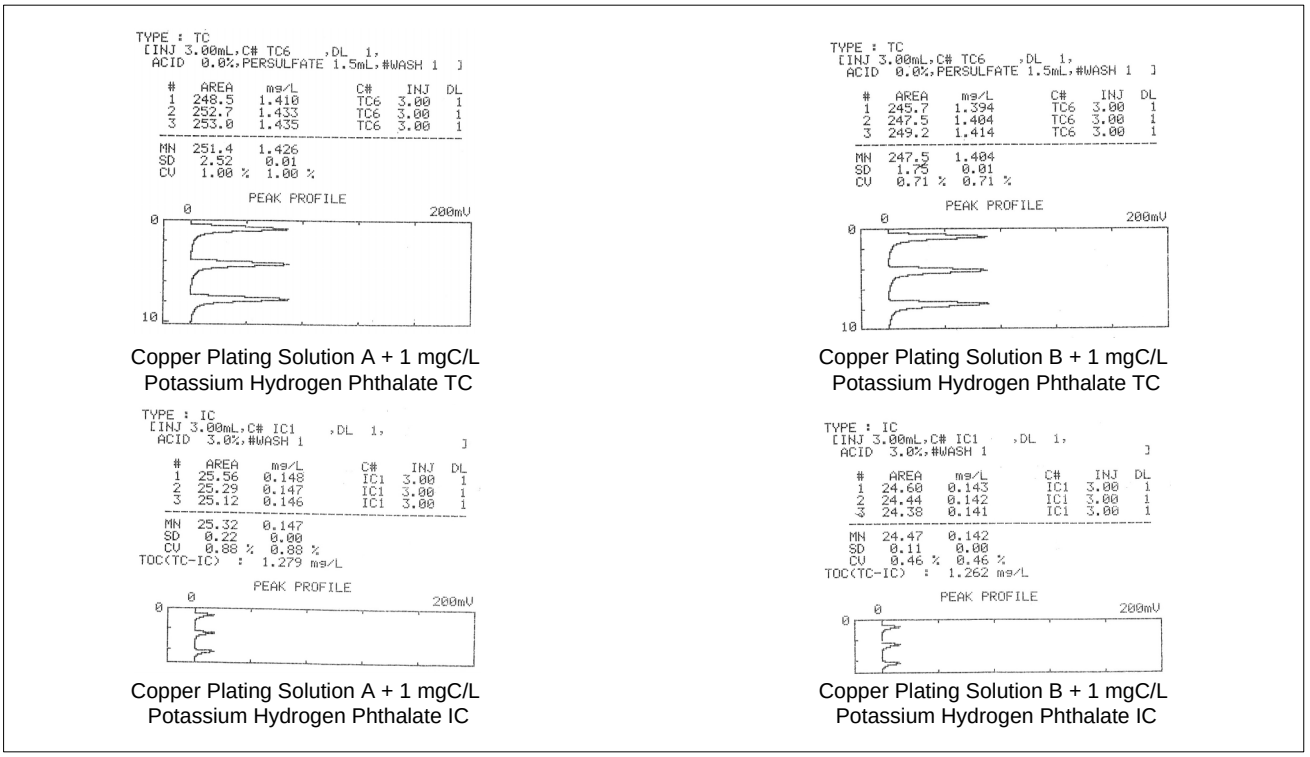
The recovery rate was obtained as follows:
Recovery rate [%] = (TOC value of recovery solution - TOC value of plating solution obtained in ①/Added TOC value

The results of the recovery tests performed on the two types of copper plating solution are shown in Fig.2 and Table 2. It can be seen that a recovery rate of almost 100 % was obtained for both solutions and that the TOC was measured accurately without the influence of sample matrix, such as copper sulfate.

<Measurement Conditions>
Analyzer : Shimadzu Wet oxidation TOC analyzer TOC-Vws
Measurement item : TOC (TC-IC)
Sample : Solution obtained by adding potassium hydrogen phthalate to copper plating solution (copper sulfate: approx. 13 %) to a concentration of 1 mgC/L

Table 2 Recovery Test for TOC in Copper Plating Solution

Sample name	TC [mgC/L]	IC [mgC/L]	TOC (TC-IC) [mgC/L]	Recovery rate [%]
Copper plating solution A + 1 mgC/L potassium hydrogen phthalate	1.426	0.147	1.279	98.8
Copper plating solution B + 1 mgC/L potassium hydrogen phthalate	1.404	0.142	1.262	101



Copper Plating Solution A + 1 mgC/L Potassium Hydrogen Phthalate TC

Copper Plating Solution B + 1 mgC/L Potassium Hydrogen Phthalate TC

Copper Plating Solution A + 1 mgC/L Potassium Hydrogen Phthalate IC

Copper Plating Solution B + 1 mgC/L Potassium Hydrogen Phthalate IC

Fig. 2 Recovery Test for TOC in Copper Plating Solution

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Printed in Japan 3100-07601-10A-IK