

# Application News

## No.045

### Total Organic Carbon Analysis

## Measurement of TOC in Electroplating Solution by TOC-L<sub>CSH</sub>

Plating solution that is used in the nickel and copper electroplating process typically contains organic additives. Because these organic additives can affect plating quality, it is important to manage these additive concentrations to ensure that product quality is maintained. Since a TOC analyzer can be used to manage the concentrations of organic material in plating solution, it can be utilized for quality management of electroplated products.

As the salt concentration in plating solutions is typically more than just a few percent, this could adversely affect direct measurement using a typical combustion catalytic oxidation type TOC analyzer. Therefore, the sample must be diluted before measurement, and because the Shimadzu TOC combustion catalytic oxidation type analyzer is equipped with an automatic dilution feature, high-salt-concentration samples can be measured by automatically diluting the sample.

Here, we introduce an example of measurement of a nickel plating solution containing nickel sulfamate using the Shimadzu TOC-L<sub>CSH</sub> analyzer.

### ■ TOC Spike Test with Nickel Electroplating Solution

We conducted TOC measurement of a nickel plating solution (new, unused solution) in addition to two solutions prepared by spiking this solution with potassium hydrogen phthalate as an organic substance, at carbon concentrations of 50 mgC/L and 100 mgC/L, respectively. The results of these analyses are shown in Fig. 1 and Table 1.

We calibrated the instrument using aqueous solutions of potassium hydrogen phthalate at concentrations of 0 mgC/L and 5 mgC/L (5 mg/L carbon concentration), and generated a calibration curve. To eliminate the influence of the carbon component in the distilled water used to prepare the standard solutions, the calibration curve was shifted before use so that it passed through the origin.

Although measurement was conducted after diluting the sample 50-fold using distilled water, it is clear that the TOC-added sample was measured with excellent accuracy.

#### Measurement Conditions

|                   |                                                                                                                                                                                                                                            |
|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Analyzer          | : Shimadzu TOC-L <sub>CSH</sub> Combustion Catalytic Oxidation Type Analyzer                                                                                                                                                               |
| Catalyst          | : Standard sensitivity catalyst                                                                                                                                                                                                            |
| Injection Volume  | : 100 µL                                                                                                                                                                                                                                   |
| Measurement Item  | : TOC (= NPOC: TOC by acidification/sparging)                                                                                                                                                                                              |
| Calibration Curve | : 2-point calibration curve using 0 – 5 mgC/L potassium hydrogen phthalate aqueous solution                                                                                                                                                |
| Samples           | : (1) Nickel sulfamate plating solution<br>(2) Solution (1) spiked with potassium hydrogen phthalate to obtain concentration of 50 mgC/L<br>(3) Solution (1) spiked with potassium hydrogen phthalate to obtain concentration of 100 mgC/L |
| Dilution factor   | : 50 times                                                                                                                                                                                                                                 |

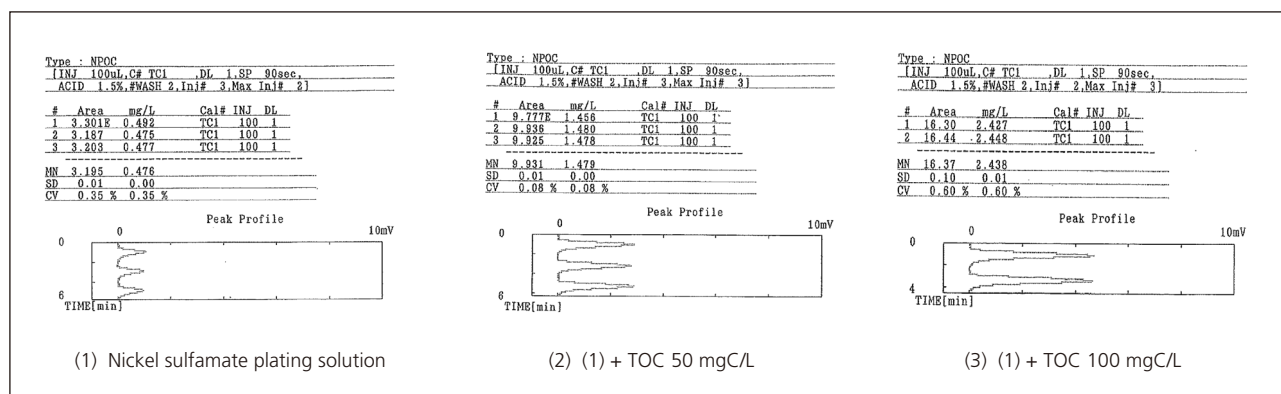


Fig. 1 Measurement Data from TOC Spike Test in Nickel Electroplating Solution

**Table 1 Measurement Data of TOC Spike Test in Nickel Electroplating Solution**

| Sample Name                                               | TOC Value [mgC/L] in 50-Fold Dilution | TOC Value [mgC/L] Corrected Using Dilution Factor |
|-----------------------------------------------------------|---------------------------------------|---------------------------------------------------|
| (1) Nickel sulfamate plating solution (previously unused) | 0.476                                 | 23.8                                              |
| (2) (1) + TOC 50 mgC/L                                    | 1.48                                  | 74.0                                              |
| (3) (1) + TOC 100 mgC/L                                   | 2.44                                  | 122                                               |

**Table 2 Measurement Data of TOC in Nickel Electroplating Solution**

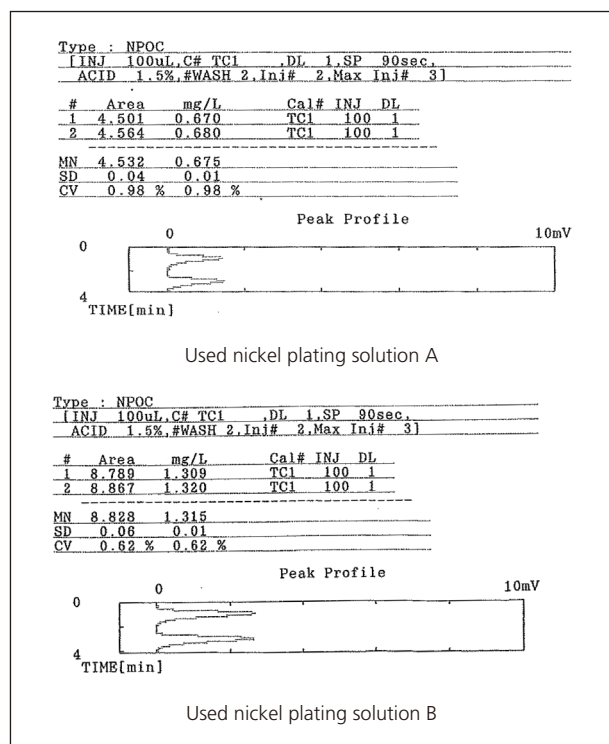
| Sample Name                                               | TOC Value [mgC/L] in 50-Fold Dilution | TOC Value [mgC/L] Corrected Using Dilution Factor |
|-----------------------------------------------------------|---------------------------------------|---------------------------------------------------|
| (1) Nickel sulfamate plating solution (previously unused) | 0.476                                 | 23.8                                              |
| Used nickel plating solution A                            | 0.675                                 | 33.8                                              |
| Used nickel plating solution B                            | 1.315                                 | 65.8                                              |

**■ Measurement of TOC in Used Nickel Electroplating Solution**

Next, we conducted TOC measurement of a nickel plating solution that was used in a mass production line. The results are shown in Fig. 2 and Table 2. The TOC value in the used plating solution was greater than that in the new, unused solution. These results demonstrate that TOC measurement can be used for management of the organic substance concentration in electroplating solution.

**Measurement Conditions**

|                   |                                                                                             |
|-------------------|---------------------------------------------------------------------------------------------|
| Analyzer          | : Shimadzu TOC-LcSH Combustion Catalytic Oxidation Type Analyzer                            |
| Catalyst          | : Standard sensitivity catalyst                                                             |
| Injection Volume  | : 100 µL                                                                                    |
| Measurement Item  | : TOC (= NPOC: TOC by acidification/sparging)                                               |
| Calibration Curve | : 2-point calibration curve using 0 – 5 mgC/L potassium hydrogen phthalate aqueous solution |
| Sample            | : Nickel sulfamate plating solution                                                         |
| Dilution Factor   | : 50 times                                                                                  |



**Fig. 2 Measurement Data of TOC in Nickel Electroplating Solution**