



# Determination of the suppressor additive in acid copper plating bath

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## Introduction

Copper electroplating systems are used for the deposition of copper on semiconductor wafers.<sup>1,2</sup> The primary components of an acid copper plating bath are copper sulfate, sulfuric acid, and hydrochloric acid. A proprietary suppressor additive is used to influence the quality of copper deposition. Cyclic voltammetric stripping (CVS) is widely used to measure the combined effect of the additives and by-products on the plating quality.<sup>3-6</sup> However, CVS is not able to detect individual components, by-products, or compounds that are not electrochemically active.

Liquid chromatography has been successfully applied to the determination of chloride<sup>7</sup> and the proprietary accelerator additive<sup>8</sup> in the acid copper plating bath. Because maintaining the level of the suppressor within the recommended operating range ensures the quality of the fill (copper deposition), we developed a method to determine the suppressor additive. This application note describes the use of the Thermo Scientific™ Dionex™ IonPac™ NS1 column with evaporative light-scattering detection to determine two different proprietary suppressors in acid copper plating baths.

## Experimental

### Equipment

- Thermo Scientific™ Dionex™ DX-600 Liquid Chromatography System\* consisting of:

- GP50 Gradient Pump
- AS50 AutoSelect Autosampler

\* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ system.

- Polymer Labs PL-ELS 1000 Evaporative Light Scattering Detector (ELSD)
- Thermo Scientific™ Dionex™ UCI-100 Universal Chromatography Interface
- Column: Dionex IonPac NS1 Analytical, 4 × 250 mm (P/N 035321)
- 100 µL PEEK sample loop (P/N 42951)
- Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstation, Version 6.0 or higher
- Gas fittings needed for connecting a nitrogen gas regulator with the ELSD:
  - Fitting, elbow 5/32 in. tube × 1/4 in. pipe thread, press fitting (P/N 049272)
  - Fitting, union 1/4 in. × 5/32 in. tube, press fitting (P/N 049267)
  - Filter for gas inlet line (P/N 215428)

### Reagents and standards

- Deionized water (DI H<sub>2</sub>O), Type I reagent grade, 18.2 MΩ·cm resistance or better
- Acetonitrile, HPLC grade (Honeywell Burdick & Jackson™ or equivalent)
- Acid Copper Plating Bath Make-Up solution (copper sulfate, sulfuric acid, and chloride)
- Enthone and Shipley suppressor additives or equivalent

### Solutions and reagents

#### Make-Up Solution

The acid copper bath Make-Up solution comes premixed with copper sulfate, sulfuric acid, and hydrochloric acid.

### Suppressor Solutions

The suppressor solutions are spiked into the Make-Up solution at the concentrations recommended by the manufacturer.

### System preparation and setup

The PLS-ELS 1000 is the evaporative light-scattering detector used for the detection of the suppressor. The ELSD requires a supply of nitrogen (98% purity or better) with an operating range of 0–100 psi (4–6.7 Bar). An inline filter is used to trap particulate matter. The solvent is evaporated as it passes through the instrument and then exits through the rear of the unit. This exhaust must be sent to a fume hood or similar solvent disposal unit. For more information about the installation of the ELSD, see the *Operator's Manual for the PL-ELS 1000 Evaporative Light Scattering Detector*.<sup>9</sup>

The Dionex UCI-100 Universal Chromatography Interface is used to interface the ELSD with the Dionex PeakNet 6 chromatography data system. The output of the ELSD is an electrical voltage signal that is digitized by the UCI-100. The data system computer is connected to UCI-100 via a USB connection or via a private LAN. The procedure for installing the UCI-100 and connecting it to the Dionex PeakNet 6 chromatography data system is described in the *Universal Chromatography Interface UCI-100 Operating Instructions*.

The Dionex UCI-100 is used to acquire the data signal from the ELSD, but the Dionex UCI-100 does not control the ELSD. The ELSD is controlled from the removable handset of the detector or through the Polymer Labs PL-ELS Control Software. The key operating parameters of the ELSD detector are the nebulizer flow rate, evaporator temperature and nebulizer temperature. The nebulizer flow rate determines the flow of nitrogen gas used to evaporate the eluent. The evaporator temperature should be set high enough to evaporate the eluent without having a detrimental effect on analyte detection. The nebulizer temperature is the least-often adjusted parameter and is set at a temperature higher than that experienced by the columns.

Connect the outlet of the Dionex IonPac NS1 column to the eluent inlet of the ELSD. Turn on the nitrogen gas pressure to a pressure of about 60 psi or greater. Switch on the detector and set the evaporation temperature to

80°C, nitrogen gas flow rate to 1 L/min, and nebulizer temperature to 75°C. Initiate heating of the detector by pressing the RUN key. Wait for the detector to arrive at the appropriate temperature. After the unit has equilibrated, the baseline should be checked to ensure that the baseline peak-to-peak noise is less than 200 µV. Turn on the eluent flow and check the baseline noise. It should be less than 1 mV. The instrument is now ready to run. For more details on setup and operation, consult the *Operator's Manual for the PL-ELS 1000 Evaporative Light Scattering Detector*.<sup>9</sup>

## Results and discussion

The determination of organic additives in acid copper plating baths requires specialized instrumentation. The detection of the suppressor is hampered by the excess of sulfuric acid and copper sulfate. A typical high performance liquid chromatograph (HPLC) would not be suitable for this analysis, because the highly acidic plating bath samples (10% sulfuric acid) corrode the stainless steel fluid pathway. For this reason, a liquid chromatography system that has a PEEK flow pathway was used. This inert polymer is resistant to the corrosive effects of the copper plating bath.

A silica-based reversed-phase column would normally be considered for the separation of this analyte. However, a silica column packing is not suitable for use with this highly acidic sample matrix. Instead, a polymeric reversed-phase Dionex IonPac NS1 column was used because it is stable over a wide pH range of 0–14. Chromatographic conditions were optimized for separating two different suppressors from the acid copper bath using a gradient from 40–90% acetonitrile. Gradient conditions are listed in Table 1.

### Conditions

Eluent Flow Rate:	1.0 mL/min
Detection:	Evaporative Light Scattering
Evaporator Temperature:	80 °C
Nebulizer Temperature:	75°C
Nitrogen Flow Rate:	1.0 L/min
Detector Output:	10 volt full scale
Sample Volume:	100 µL

**Table 1. Gradient program.**

Time (min)	V	% E1	% E2	Description
-5	Load	60	40	Load Sample
0	Inject			Begin data acquisition
2	Inject	60	40	Gradient from 40–90% acetonitrile
7	Inject	10	90	End gradient. Hold at 90% acetonitrile
10	Inject	10	90	Gradient from 90–40% acetonitrile
15	Inject	60	40	End data acquisition

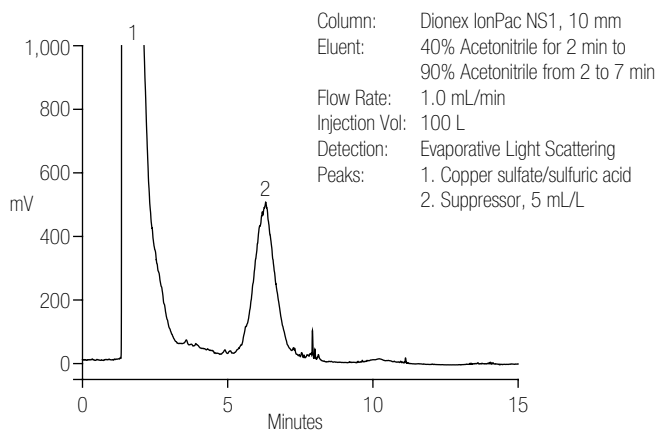
V = Injection valve

E1 = Deionized water

E2 = Acetonitrile

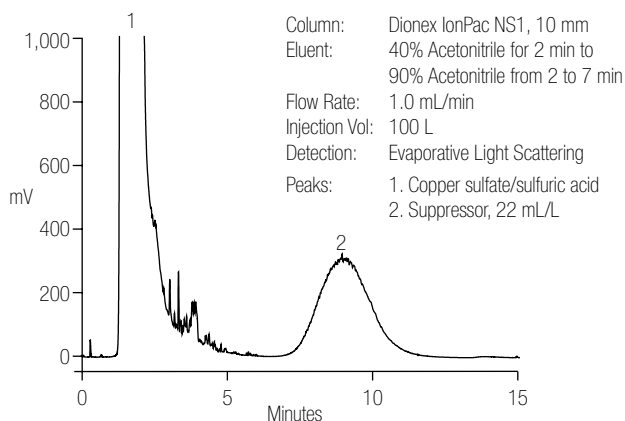
The determination of the suppressor additives is challenging because they do not have a strong chromophore, and therefore cannot be easily determined by UV photometric detection. ELSD was explored as an alternative detector.<sup>10–12</sup> With ELSD, the analytes of interest are separated on a column and the effluent is passed through a nebulizer. The mobile phase evaporates and a plume of nonvolatile solute particles forms. A light beam passes through the analyte particles and the scattered radiation is detected. The analyte response is proportional to its concentration.

Prior to detection with the ELSD, the suppressor was separated from the other bath components using a Dionex IonPac NS1-10 µm polymeric reversed-phase column. Figure 1 shows the chromatogram obtained for a fresh plating bath sample containing 5 mL/L Enthone suppressor. The suppressor peak at 6 min is well resolved from the large matrix peak at 2 min. The recommended operating range for the Enthone suppressor is 4–12 mL/L in the copper plating bath. Using this range, a coefficient of determination ( $r^2$ ) of 0.9993 was calculated for a three-level calibration curve.



**Figure 1. Determination of enthone suppressor in acid copper plating bath before electrolysis.**

The Shipley suppressor can also be determined using this method (Figure 2). The suppressor is well resolved from the matrix peak and elutes at 9 min. The recommended operating range for the S-2001 Shipley suppressor is 20–25 mL/L in the copper plating bath. Using this range, a coefficient of determination ( $r^2$ ) value of 0.9798 was calculated for a three-level calibration curve.



**Figure 2. Determination of Shipley suppressor in acid copper plating bath before electrolysis.**

## Maintenance

On a daily basis, after your analysis is complete, turn off the eluent pump and put the ELSD into “Standby” mode, and turn off the power. Once a month it is beneficial to clean the evaporator tube to prevent the buildup of nonvolatile materials. To clean the detector, set the evaporator to 150°C, the nebulizer temperature to 90°C and the gas flow to 2 L/min. Use a deionized water eluent at 1 mL/min. Use air rather than nitrogen for the nebulizing gas and leave at the set temperatures in the “Run” mode for approximately 3–4 hours. Then run the detector with heat, but without eluent flow for 30 min.

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