The chloride concentration of an acid copper plating bath is critical to the quality of copper deposition. Ion chromatography (IC) with eluent generation and high-capacity anion-exchange columns provides a convenient method to accurately monitor the chloride concentration of this very acidic and highly ionic sample.

Acid copper plating baths are used for deposition of copper on semiconductor wafers. Monitoring chloride concentration is of interest because it plays an important role in the quality of copper deposition. Compared with standard wet chemical techniques, IC offers improved speed and accuracy for this analysis. An acid copper bath typically contains copper sulfate, sulfuric acid, hydrochloric acid, and a variety of proprietary additives. Figure 1 shows an analysis of a 25-μL sample of copper plating bath diluted 1:100. Chloride is detected by suppressed conductivity and the EG40 eluent generator is used to prepare the 30 mM potassium hydroxide eluent on-line. The analyst only needs to add water to the chromatography system. Chloride is separated from the excess of sulfate present in the copper plating bath using the IonPac AS15, a high-capacity ion-exchange column. This application update describes the setup and procedure to determine chloride in a copper plating bath.

Figure 1: Chromatogram from an analysis of a 25-μL sample of copper plating bath diluted 1:100.

### Equipment
Dionex DX-600 ion chromatography system consisting of:
- GP50 gradient pump
- CD25 conductivity detector
- EG40 eluent generator system with EluGen® EGC-KOH cartridge (P/N 053921)
- LC20 chromatography enclosure equipped with Rheodyne model 9126
- Injector, PEEK, rear loading (P/N 052291)
- Columns: IonPac AS15 analytical, 250 mm × 4 mm (P/N 053940) and IonPac AG15 guard, 50 mm × 4 mm (P/N 053942)
- Trap column: ATC-1 Trap, 24 mm × 9 mm (P/N 037151)
- Suppressor: ASRS®-ULTRA, 4 mm (P/N 053947)
- 25-μL PEEK sample loop (P/N 042857)
- PeakNet® Chromatography Workstation

### Results
The nominal concentration of chloride in the copper plating bath is 45 mg/L (ppm). The method detection limit (MDL) for this procedure is 6 mg/L chloride. (This is based on an MDL of 0.06 mg/L for a 25-μL injection of a sample diluted 1:100.) Because a high-capacity anion-exchange column was used, only a small dilution is required instead of a larger, possibly less-accurate dilution.

To verify proper quantification of chloride in the copper plating bath matrix, increasing concentrations of chloride were spiked in the deionized water used to dilute the copper bath 1:100. This fresh copper plating bath sample contained three proprietary additives. A coefficient of determination ($r^2$) value of 0.9983 was calculated for a three-level calibration curve with three replicates at each level. The three concentration levels were: 1) unspiked bath sample, 2) spike at 0.5 mg/L chloride, and 3) spike at 1.0 mg/L chloride. An average measured concentration of chloride in this sample was 47.2 ± 1.2 mg/L (based on the undiluted bath) for 21 replicate injections.

This method has been demonstrated to give reliable quantification of chloride for more than 500 injections.