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Determination of Chloride in Acid Copper Plating Bath

INTRODUCTION

Ion chromatography (IC) provides a convenient method for the determination of chloride in acid copper plating baths. These 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 to 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- μ L 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. Chloride is separated from the excess of sulfate present in the copper plating bath. This Application Update describes the setup and procedure to determine chloride in a copper plating bath using the IonPac[®] AS15 column.

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, 4 x 250 mm (P/N 053940)
IonPac AG15 guard, 4 x 50 mm (P/N 053942)

Trap Column: ATC-1 Trap, 9 x 24 mm (P/N 037151)

Suppressor: ASRS[®]-ULTRA, 4 mm (P/N 053947)

25- μ L PEEK sample loop (P/N 042857)

PeakNet[®] Chromatography Workstation

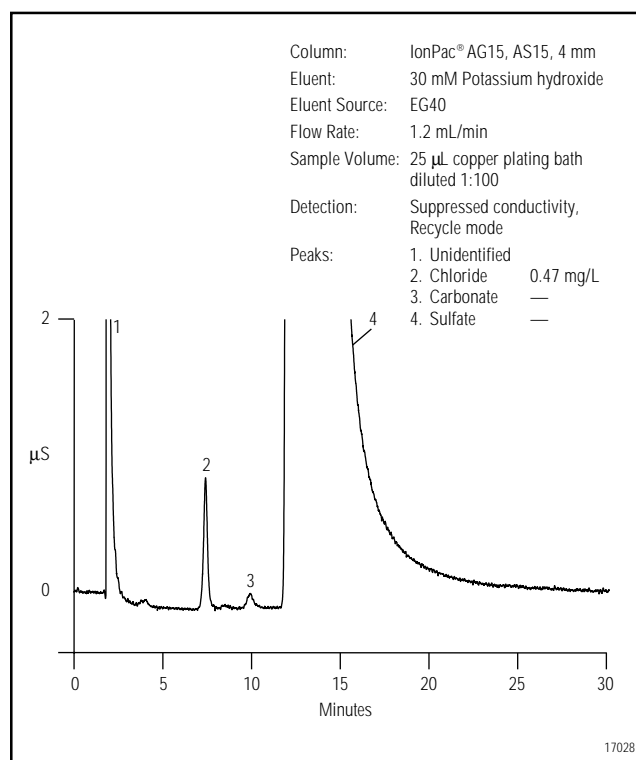


Figure 1. Determination of chloride in acid copper plating bath.

REAGENTS AND STANDARDS

Deionized water (DI H₂O), Type I reagent grade,
17.8 MΩ-cm resistance or better

Sodium hydroxide 50% w/w aqueous solution
(Fisher Scientific)

Potassium hydroxide 45% w/w aqueous solution
(Fisher Scientific; optional instead of
sodium hydroxide)

Chloride standard 1000 mg/L, 100 mL
(Dionex P/N 037159)

SAMPLE PREPARATION

Dilute the copper plating bath 1:100 with
deionized water.

STANDARD

Dilute the 1000 mg/L chloride standard to bracket
the expected chloride concentration.

CONDITIONS

Column: IonPac AG15, AS15, 4 mm

Eluent: 30 mM Potassium hydroxide

Eluent Source: EG40

Flow Rate: 1.2 mL/min

Sample Volume: 25 µL of copper plating bath diluted
1:100

Detection: Suppressed conductivity, Recycle mode

EG40 Offset

Volume: 0 µL

Pump Program:

Time (min)	Flow (mL/min)	%A	Valve	EG40 Conc. (mM)	Comments
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Initial	1.2	100	Load	30	Load sample loop
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0.00	1.2	100	Inject	30	Inject
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30.00	1.2	100	Load	30	End acquisition
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ASRS Current Setting: 100 mA

Expected Background

Conductivity: 1 µS

Expected System

Backpressure: 16.5 MPa (2400 psi)

ATC Regeneration Solution: 2 M Sodium Hydroxide

Dilute 160 g of 50% (w/w) sodium hydroxide with
degassed, deionized water (with a specific resistance of
17.8 MΩ-cm or greater) to a final weight of 1080 g in an
eluent bottle. Avoid the introduction of carbon dioxide
from air. (2 M potassium hydroxide can be used instead
of 2 M sodium hydroxide. Preparation is the same as
above except that 249 g of 45% potassium hydroxide is
used for a final weight of 1090 g.)

SYSTEM PREPARATION AND SETUP

Prepare the ASRS according to the *Quickstart
Instructions for the ASRS-ULTRA* (Document
No. 031368). Prepare the ATC for use by rinsing it with
200 mL of 2 M KOH or 2 M NaOH at 2.0 mL/min. This
can be done off-line (without the GP50) by pressurizing
an eluent bottle with helium using 0.030-in. (0.75-mm)
i.d. PEEK tubing. Rinse the ATC with deionized water at
2.0 mL/min for 20 minutes. Install the EGC-OH EluGen
cartridge according to the instructions in the Operator's
Manual for the EG40 Eluent Generator System (Docu-
ment No. 031373). Place the 4-mm ATC between the
GP50 outlet and the KOH cartridge inlet.

PERFORMANCE CHARACTERISTICS

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.) The MDL was calculated
using three times the noise. Noise was measured to be
17.5 ± 5.8 nS for an average of ten 1-minute sections of
a representative baseline signal.

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 (r²) 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 over 500 injections. Retention time for chloride can gradually decrease over time because of a loss of column capacity, probably due to bath components concentrating on the column. Depending on the nature of the contaminants it might be possible to clean the column. See the *Installation Instructions and Troubleshooting Guide for the IonPac AS15* (Document No. 031362) for more information about column cleanup protocols.

SUPPLIER

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