# Determination of Additives and Byproducts in an Acid Copper Plating Bath by Liquid Chromatography

## INTRODUCTION

Copper electroplating systems are used for the deposition of copper on semiconductor wafers.[1,2] The primary components of an acid copper plating bath are copper sulfate, sulfuric acid, and hydrochloric acid; a variety of proprietary additives are used to influence the quality of copper deposition.[3,4] As the bath ages, certain byproducts are formed as a result of the plating process.

Cyclic voltammetric stripping (CVS) is widely used to measure the combined effect of the additives and byproducts on the plating quality.[5-8] However, CVS is not able to detect individual components or compounds that are electrochemically inactive. Chromatography can be used to quantitatively measure individual additives and byproducts.[9-11] Tracking the levels of these components ensures the quality of the fill. This Application Note describes the use of the IonPac® NS1 column with absorbance detection to determine additives and byproducts in acid copper plating baths.

## EQUIPMENT

Dionex DX-600 Liquid Chromatography System consisting of:

- GP50 Gradient Pump
- AD25 Absorbance Detector or PDA-100 Photodiode Array Detector
- AS50 Autosampler, PEEK (polyetherether ketone) with chromatography compartment

PeakNet® Chromatography Workstation

10-µL sample loop

500-µL sample loop

Optional: 0.020-in. (0.50-mm) orange PEEK tubing or 0.030-in. (0.75-mm) green PEEK tubing to make sample loops

## REAGENTS AND STANDARDS

Deionized water (DI $H_2O$), Type I reagent grade, 17.8 MΩ-cm resistance or better

Sulfuric acid, trace metal grade (J.T. Baker Instra-Analyzed or equivalent)

Acetonitrile, HPLC grade (Burdick & Jackson or equivalent)

Acid copper plating bath (Copper sulfate, sulfuric acid, and chloride; Enthone-OMI or other)

Proprietary additives (Enthone-OMI or other)

## PREPARATION OF SOLUTIONS AND REAGENTS

### Makeup Solution

The acid copper bath makeup solution comes premixed with copper sulfate, sulfuric acid, and hydrochloric acid.

### Standard Solutions

Additives are spiked into the makeup solution at the concentrations recommended by the manufacturer.

### 1 N Sulfuric Acid Eluent Stock Solution

Weigh out 50.04 g of 98% reagent grade sulfuric acid. Carefully add this amount to a 1-L flask containing about 500 mL of deionized water. Dilute to the mark and mix thoroughly.

*Caution: Use extreme care when handling sulfuric acid. Avoid all contact with exposed skin. The use of eye protection, proper gloves, and a fume hood is an absolute necessity. Consult the Material Safety Data Sheet (MSDS) for more specific details about protective equipment, reactivity, and health effects.*

#### 100 mN Sulfuric Acid Eluent

Pipette 100 mL of the 1.0 N sulfuric acid stock solution into a 1-L volumetric flask. Dilute to 1 L using deionized water.

#### 150 mN Sulfuric Acid Eluent

Pipette 150 mL of the 1.0 N sulfuric acid stock solution into a 1-L volumetric flask. Dilute to 1 L using deionized water.

#### 10% Acetonitrile in 150 mN Sulfuric Acid

Pipette 150 mL of the 1.0 N sulfuric acid stock solution into a 1-L volumetric flask. Add approximately 500 mL of degassed deionized water. Add 100 mL of acetonitrile and mix until all components are in solution. Dilute to a final volume of 1 L using degassed, deionized water.

## *SYSTEM PREPARATION AND SET-UP*

Two gradient methods have been developed for the determination of the bath additives and byproducts. One method is a steep gradient method from 5% to 90% acetonitrile; the other is a shallow gradient from 0.25% to 9% acetonitrile. The steep gradient is used to determine the Enthone Accelerator and B1 Leveler additives. The shallow gradient method is an optimized separation of the two Accelerator components and byproducts.

#### Chromatographic Conditions for Steep Gradient

| | |
|---|---|
| Columns: | IonPac NS1 Analytical, 10 µm, 4 x 250 mm<br>IonPac NG1 Guard, 10 µm, 4 x 35 mm |
| Eluent Flow Rate: | 1.0 mL/min |
| Detection: | UV, 190 nm |
| Sample Volume: | 500 µL |
| Expected System Backpressures: | 7.6 MPa (1100 psi) for 5% Acetonitrile/95 mN sulfuric acid<br>4.4 MPa (650 psi) for 90% Acetonitrile/10 mN sulfuric acid |

#### Steep Gradient Program

V = Injection valve

E1 = 100 mN Sulfuric acid

E2 = Acetonitrile

| Time | V | % E1 | % E2 | Description |
|---|---|---|---|---|
| 0 min | Load | 95 | 5 | Begin (15) min. equilibration, load sample |
| 15 | Inject | 95 | 5 | Inject sample, begin data acquisition |
| 35 | Inject | 10 | 90 | End gradient, end data acquisition, begin (2) min. ramp back to initial conditions |
| 37 | Inject | 95 | 5 | |

#### Chromatographic Conditions for Shallow Gradient

| | |
|---|---|
| Columns: | IonPac NS1 Analytical, 10 µm, 4 x 250 mm<br>IonPac NG1 Guard, 10 µm, 4 x 35 mm |
| Eluent Flow Rate: | 2.0 mL/min |
| Detection: | UV, 246 nm or 200 to 325 nm with PDA |
| Sample Volume: | 10 or 500 µL |
| Expected System Backpressure: | 13.1 MPa (1900 psi) |

#### Shallow Gradient Program

V = Injection valve

E1 = 150 mN Sulfuric acid

E2 = 10% Acetonitrile in 150 mN sulfuric acid

| Time | V | % E1 | % E2 | Description |
|---|---|---|---|---|
| 0 min | Load | 97.5 | 2.5 | Initial |
| 0.1 | Inject | 97.5 | 2.5 | Inject sample, start gradient |
| 2.5 | Inject | 95 | 5 | |
| 18 | Inject | 10 | 90 | |
| 20 | Inject | 97.5 | 2.5 | End gradient |
| 22 | Inject | 97.5 | 2.5 | Return to initial conditions |

Sample injection volumes can be varied according to the analysis requirements. For the shallow gradient, a 500-µL injection gives sensitivity to 1.67 mL/L Accelerator and 0.23 mL/L B1 Leveler. This injection volume can be decreased if the detection limits are higher. For the steep method, an injection volume of 10 µL gives the best resolution of the early eluting (2.5–6 min) peaks from the matrix peak. A 500-µL injection volume gives better sensitivity for the byproduct peaks that elute near the first Accelerator peak (~ 10 min).

Choose the method and sample injection volume that best suits the analysis requirements. Make a sample loop by cutting the appropriate length of PEEK (polyetherether ketone) tubing. See Table 1 for a list of loop volume and corresponding tubing lengths. For example, to make a 500-µL loop, use 43-in. (109.7-cm) of 0.03-in. (0.75-mm) i.d. PEEK tubing. The volume of a loop can be verified by measuring the weight difference between the sample loop filled with deionized water and the empty loop. The inside diameter of tubing varies by as much as 20% (for example, 0.010 ± 0.002 in.).

**Table 1 Volume per Unit Length for Various Tubing Internal Diameters**

| Material | Color | Internal Diameter | | Estimated Volume |
|---|---|---|---|---|
| | | Inches | mm | (µL/cm) |
| PEEK | Red | 0.005 | 0.125 | 0.126 |
| PEEK | Black | 0.010 | 0.250 | 0.506 |
| PEEK | Orange | 0.020 | 0.500 | 2.022 |
| PEEK | Green | 0.030 | 0.750 | 4.550 |

The IonPac NS1 is shipped in 28% acetonitrile/ 3.0 mM tetrabuytlammonium hydroxide. Prior to use, the column should be thoroughly washed with the highest concentration of eluent for the method that will be used for analysis. Obtaining reliable, consistent, and accurate results requires eluents to be free of impurities. Chemicals, solvents, and deionized water used to prepare eluents must be of the highest purity available.

Verify proper performance by running a blank injection of unspiked acid copper makeup solution. Representative blank runs for 500-µL injections with the steep and shallow gradient methods are shown in Figures 1 and 2 respectively. The steep gradient method used a wavelength of 190 nm and the shallow gradient method is presented as a 3-D plot from 200 to 325 nm.

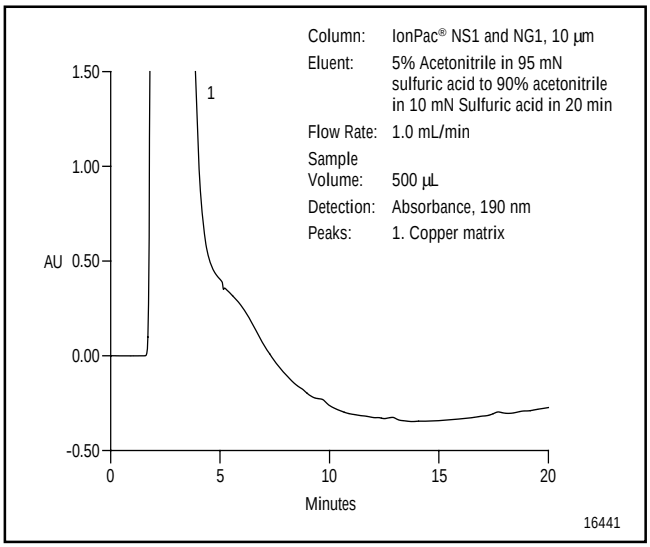


*Figure 1. Representative acid copper bath blank with steep gradient method.*

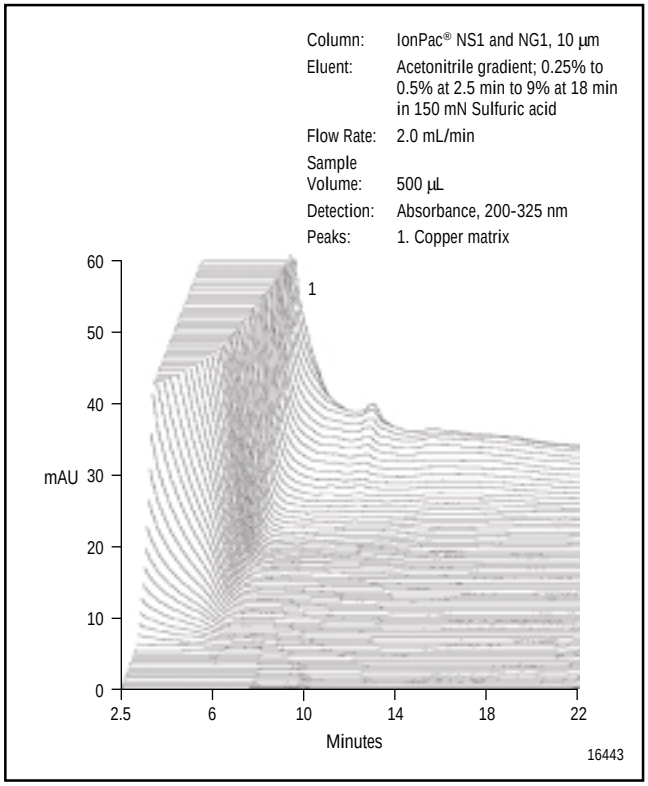


*Figure 2. Representative acid copper bath blank with shallow gradient method.*

The time axis for the 3-D plot begins at 2.5 min to avoid obscuring the display with the large matrix peak. This 3-D plot displays the absorbance output starting with the back of the plot at 200 nm and increasing to 325 nm at the front.

## DISCUSSION AND RESULTS

Analysis of acid copper plating baths is hampered by the excess of sulfuric acid and copper sulfate. This strongly acidic matrix obscures detection of the additives and byproducts. Some of these analytes are present at levels below 1 mL/L and some are not detected by absorbance because they are non-chromaphoric.

A typical high performance liquid chromatograph (HPLC) is not suitable for this analysis because these highly acidic plating bath samples (10% sulfuric acid) would corrode the instrument's stainless steel fluid pathway. For that reason, a liquid chromatography system with a flow pathway made of PEEK was used for this work. This inert polymer is resistant to the corrosive effects of the sulfuric acid in the copper plating bath and the mobile phase.

A silica-based reversed-phase column would normally be used for the separation of these neutral and polar organic analytes. However, the silica column packing is not suitable for use with this acidic sample matrix. Instead, the polymeric reversed-phase IonPac NS1 and NG1 columns were used for this study because of their wide pH operating range (0 to 14).[12] A UV spectral scan from 190 to 800 nm was run for each of the three additives to characterize their absorbance behavior. The Accelerator additive had an absorbance maxima at 246 nm; the B1 Leveler additive absorbed at the low UV from 190 to 200 nm; and the Suppressor did not have a significant absorbance signal.

Chromatographic conditions were optimized for the determination of the Accelerator and B1 Leveler additives. A method using a steep gradient from 5% acetonitrile/95 mN sulfuric acid to 90% acetonitrile/ 10 mN sulfuric acid at 1 mL/min was successful for separating the Accelerator and B1 Leveler additives. Detection was at a fixed wavelength of 190 nm. A representative chromatogram is shown in Figure 3. The large peak that elutes from ~ 2 to 5 minutes is from the copper sulfate and sulfuric acid matrix. A sample of fresh makeup bath (prior to electrolysis) was prepared by spiking 1.67 mL/L Accelerator, 2 mL/L Suppressor, and 0.23 mL/L B1 Leveler. This concentration is at one-fifth of the manufacturer's recommended operating levels. Two peaks at 5.8 and 6.5 min were attributed to the Accelerator and one peak at 17.3 min was from the B1 Leveler. The Suppressor was not detected under these conditions.

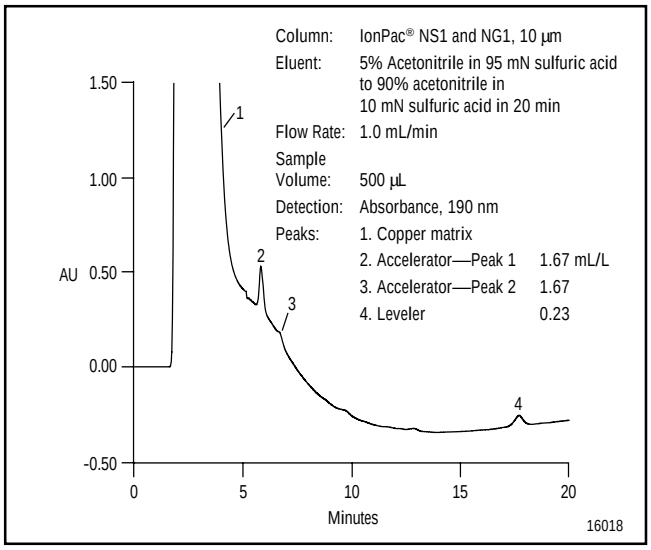


*Figure 3. Analysis of acid copper plating bath before electrolysis (steep gradient).*

To verify proper quantification of the additives, increasing concentrations of the Accelerator and Leveler were spiked into the acid copper makeup solution. Three replicate injections were made at each calibration level. Spikes of 1.67, 4.2, and 11.1 mL/L for the Accelerator and 0.23, 0.57, and 1.52 mL/L for the B1 Leveler yielded coefficients of determination ($r^2$) values of greater than 0.99. The method was validated by analyzing the same sample on two separate days. Precision for n = 18 yielded RSD values less than 10% as shown in Table 2.

**Table 2 Precision for Steep Gradient Method**

| Additive | Day | Concentration (mL/L) | RSD (%) |
|---|---|---|---|
| Accelerator Peak 1 | 1 | 1.71 ± 0.03 | 1.9 |
| | 2 | 1.70 ± 0.06 | 3.5 |
| Accelerator Peak 2 | 1 | 2.09 ± 0.20 | 9.6 |
| | 2 | 1.92 ± 0.11 | 5.6 |
| Leveler | 1 | 0.27 ± 0.01 | 6.2 |
| | 2 | 0.21 ± 0.01 | 6.9 |

A method using a shallow gradient from 0.25% to 9% acetonitrile at 2 mL/min provided better resolution of the two Accelerator peaks. A diode array detector was used for this analysis because of its ability to simultaneously gather spectral data from a range of 190 nm to 800 nm. This allowed precise determination of absorption maxima for the analytes of interest.

Figure 4 shows the PDA output for a 500-µL injection of a fresh bath spiked with 1 mL/L of Accelerator. Under these separation conditions, the two Accelerator peaks are better resolved from the matrix peak. The B1 Leveler is not detected because a higher concentration of acetonitrile is required for elution. No byproducts were detected because this sample was taken prior to electrolysis.

A wavelength of 246 nm was selected to give the best signal-to-noise ratio for the two Accelerator peaks. Figure 5 shows this single-wavelength chromatogram extracted from the PDA data.

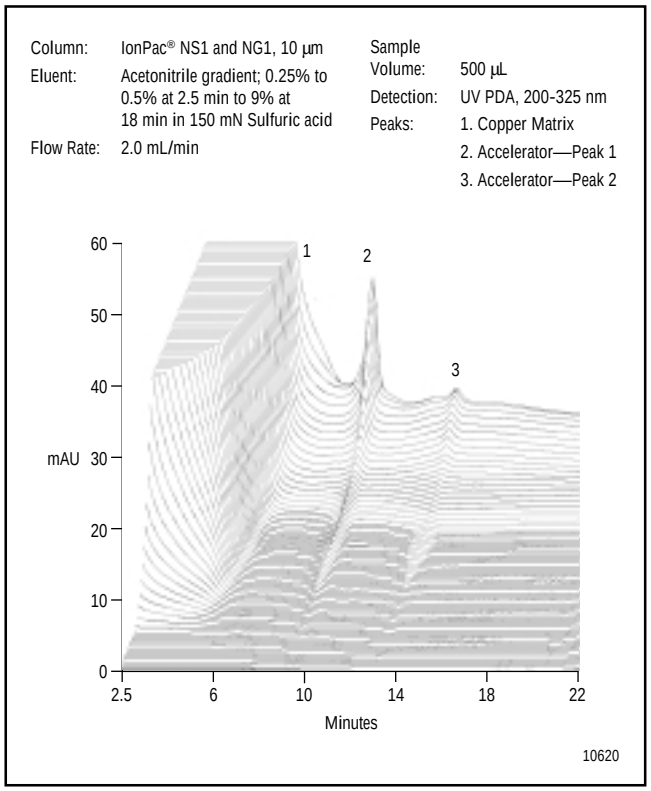


*Figure 4. Analysis of acid copper plating bath before electrolysis (shallow gradient).*

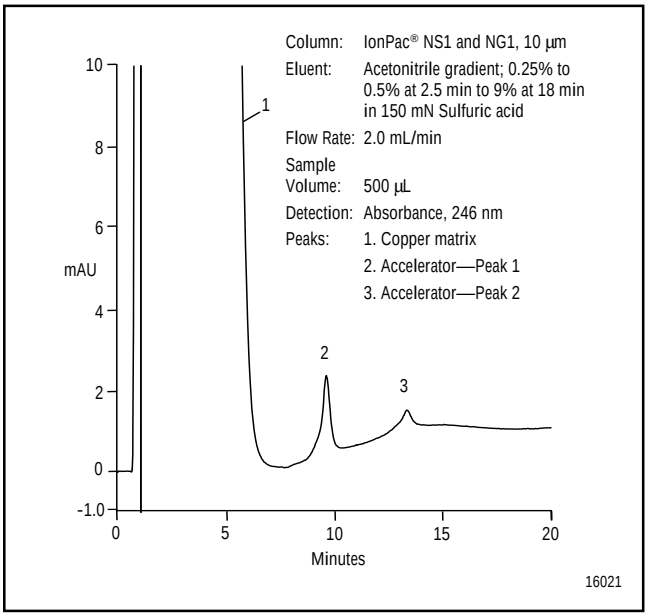


*Figure 5. Analysis of acid copper plating bath before electrolysis (shallow gradient).*

An aged bath sample was also analyzed with a 10-µL sample. This smaller injection volume reduced the size of the matrix peak as shown in Figure 6. The matrix peak would have obscured these early-eluting peaks had a 500-µL injection been used. The Accelerator Peak 1 elutes at ~ 11 min as with the 500-µL injection. Two additional species that were not present in the fresh bath sample were detected at 3.4 and 6.2 min. The retention times differ from the species found with the 500-µL injection and are therefore labeled Byproduct A and Byproduct B. Closer examination of the PDA spectra reveals a stronger signal in the lower wavelengths, especially for Byproduct A.

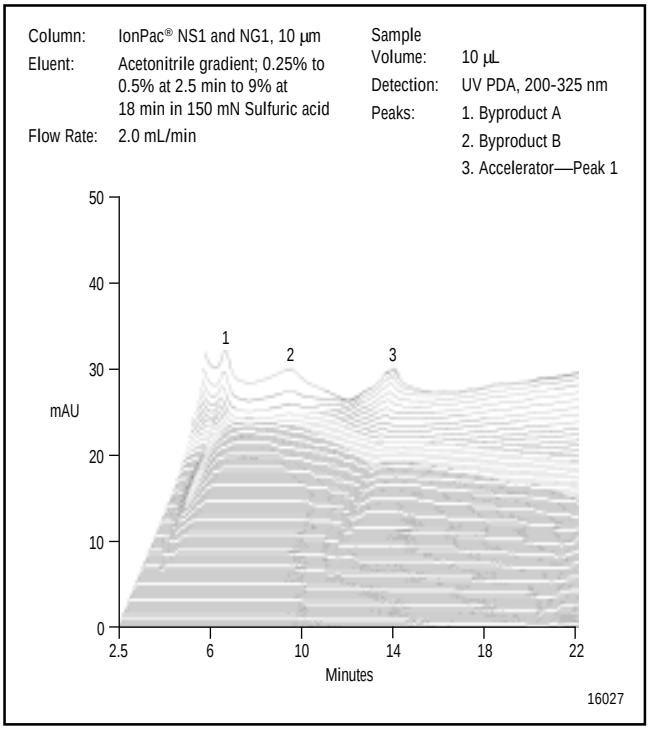


*Figure 6. Analysis of acid copper plating bath after electrolysis (shallow gradient).*

To identify the byproducts, possible candidates were generated by synthesis and by electrolyzing the additives. These compounds were spiked into the spent bath as a means of identifying the byproduct peaks. There was a good match in retention time and spectral characteristics when one of these synthesized compounds was spiked in for Byproduct A, as shown in Figure 7. In the same way, Byproduct Peak B was also identified with the spike shown in Figure 8. The area of Accelerator Peak 1 also increased in this case because it was needed for the synthesis of Byproduct Peak B.

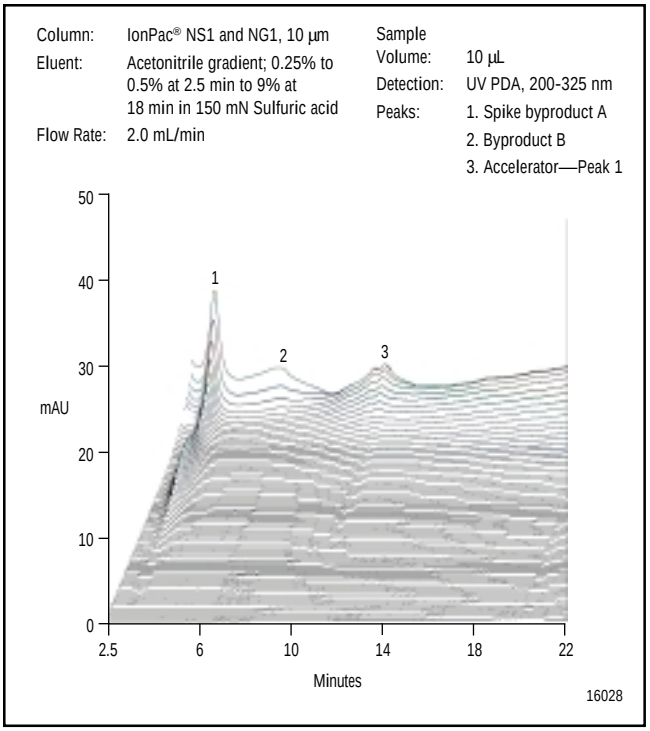


*Figure 7. Analysis of spiked acid copper plating bath after electrolysis (shallow gradient).*

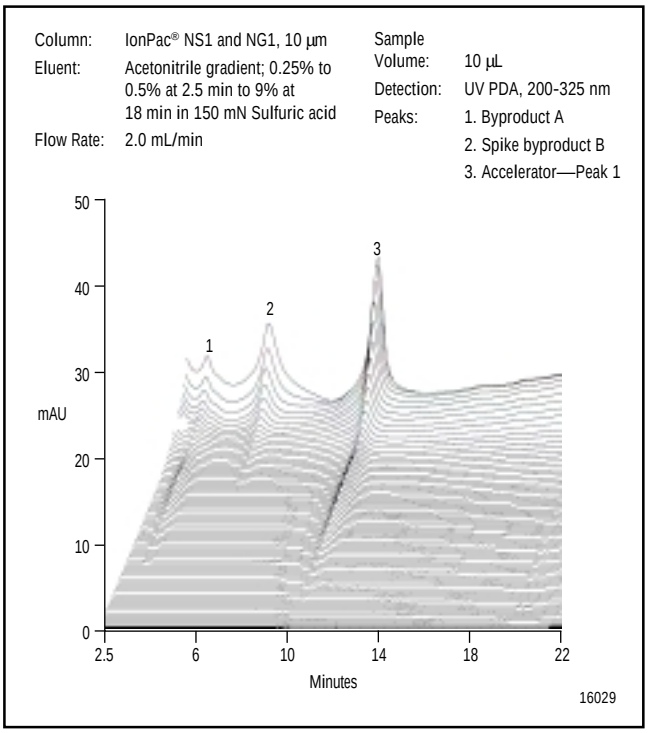


*Figure 8. Analysis of spiked acid copper plating bath after electrolysis (shallow gradient).*

## PRECAUTIONS

It is essential that the NG1 and NS1 columns have an operational concentration range of 0.25% to 95% solvent. This will ensure that the hydrophobic surfaces are wetted and maximum column performance is maintained. If the column is exposed to less than 0.25% solvent for extended time, the column packing will collapse and headspace will form in the column. This will result in a loss of efficiency because of the extra dead volume in the system. The steep gradient method is more resilient and has been shown to last for over 500 injections of 500 µL. Use of the shallow gradient method will cause degradation after 200 injections of 500 µL.

Use the following procedure to determine whether a column has developed headspace:

1. Disconnect the column for the system.
2. Carefully unscrew the inlet (top) column fitting using two open-end wrenches.
3. Remove the old bed support.
4. Turn the end fitting over and tap it against a benchtop or other hard, flat surface to remove the bed support and seal assembly.
5. If the resin does not fill the column body all the way to the top, the resin bed has collapsed, creating a headspace. The column must be replaced.

Note: The AS40 autosampler should not be used for this application due to the highly acidic nature of the samples.

## REFERENCES


1. Hurtubise, R.; Too, E.; Cheng, C. C. *Future Fab Intl*., **1998**, 243–245.
2. Lin, X. W.; Pramanik, D. *Solid State Technol.* **1998**, *41 (10)*, 63–79.
3. Plieth, W. *Electrochimica Acta*, **1992**, *37 (12)*, 2115–2121.
4. Kelly, J.J.; Tian, C.; West, A. C. *J. Electrochem. Soc.*, **1999**, *146*, 2540–2545.
5. Tench, D.; Ogden, C. *J. Electrochem. Soc.*, **1978**, *125*, 194.
6. Ogden, C.; Tench, D. *Plat. and Surf. Fin.*, **1978**, *66*, 30.
7. Haak, R.; Ogden. C.; Tench, D., *Plat. and Surf. Fin.*, **1982**, *69*, 62.
8. Freitag, W. O.; Ogden, C.; Tench, D.; White, J. *Plat. and Surf. Fin.*, **1983**, *70*, 55.
9. Reid, J.D. *Plat. and Surf. Fin.*, **1988**, 75, 108–112.
10. Heberling, S.; Campbell, D.; Carson, S. *PC Fab.*, **1989**, *12 (8)*, 72.
11. Taylor, T.; Ritzdorf, T.; Lindberg, F.; Carpenter, B. *Solid State Technol.*, **1989**, *41 (11)*, 47–57.
12. Weiss, J. *J. Chromatogr.* **1986**, *353*, 303–307.


## SUPPLIERS

Burdick & Jackson, 1653 S. Harvey St., Muskegon, MI 49442, USA. Tel: 1-800-633-7370

J.T. Baker, 222 Red School Lane, Phillipsburg, NJ 08865, USA. Tel: 1-800-582-2537



Printed on recycled and recyclable paper.

**Dionex Corporation**
1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

**Dionex Corporation**
Salt Lake City Technical Center
1515 West 2200 South, Suite A
Salt Lake City, UT
84119-1484
(801) 972-9292

**Dionex U.S. Regional Offices**

| | |
|---|---|
| Sunnyvale, CA | (408) 737-8522 |
| Westmont, IL | (630) 789-3660 |
| Houston, TX | (281) 847-5652 |
| Atlanta, GA | (770) 432-8100 |
| Marlton, NJ | (856) 596-06009 |

**Dionex International Subsidiaries**
*Austria* (01) 616 51 25 *Belgium* (32) 3-353 42 94 *Canada* (905) 844-9650 *China* (852) 2428 3282 *Denmark* (45) 36 36 90 90
*France* 01 39 30 01 10 *Germany* 06126-991-0 *Italy* (06) 66 51 50 52 *Japan* (06) 6885-1213 *The Netherlands* (0161) 43 43 03
*Switzerland* (062) 205 99 66 *United Kingdom* (01276) 691722
* Designed, developed, and manufactured under an NSAI registered ISO 9001 Quality System.

ISO 9001 REGISTERED*

LPN 1251-01 5M 6/02