Determination of additives and byproducts in an acid copper plating bath by liquid chromatography

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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 Thermo Scientific™ Dionex™ IonPac™ NS1 column with absorbance detection to determine additives and byproducts in acid copper plating baths.

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Experimental

Equipment

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

  – GP50 Gradient Pump

  – AD25 Absorbance Detector or PDA-100 Photo-diode Array Detector

  – AS50 Autosampler, PEEK™ (polyetherether ketone) with chromatography compartment

* Equivalent or improved results can be achieved using the Thermo Scientific™ Dionex™ ICS-5000⁺ HPIC™ system with a Thermo Scientific™ Dionex™ ICS-Series VWD Variable Wavelength Detector.

- Thermo Scientific™ Dionex™ 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 (Honeywell 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 setup

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:	Dionex IonPac NS1 Analytical, 10 µm, 4 × 250 mm Dionex IonPac NG1 Guard, 10 µm, 4 × 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 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:	Dionex IonPac NS1 Analytical, 10 µm, 4 × 250 mm Dionex IonPac NG1 Guard, 10 µm, 4 × 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 = 100 mN Sulfuric acid
E2 = Acetonitrile

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 (µL/cm)
		Inches	mm	
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 Dionex IonPac NS1 column 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 Figure 1 and Figure 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.
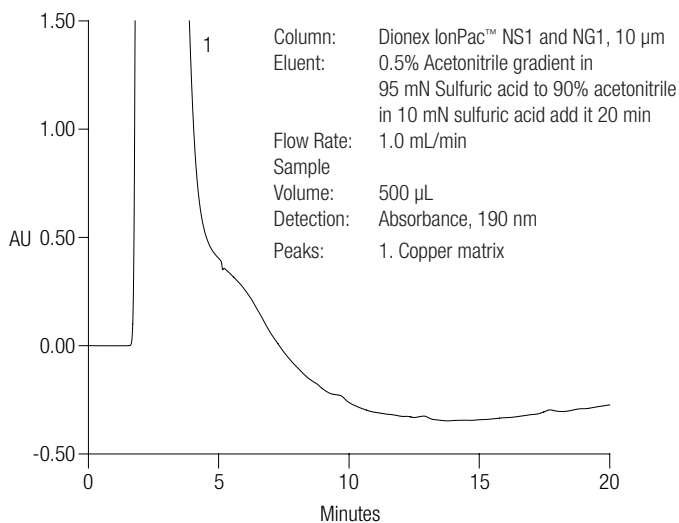

Column:	Dionex IonPac™ NS1 and NG1, 10 µm
Eluent:	0.5% Acetonitrile gradient in 95 mN Sulfuric acid to 90% acetonitrile in 10 mN sulfuric acid add it 20 min
Flow Rate:	1.0 mL/min
Sample Volume:	500 µL
Detection:	Absorbance, 190 nm
Peaks:	1. Copper matrix

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

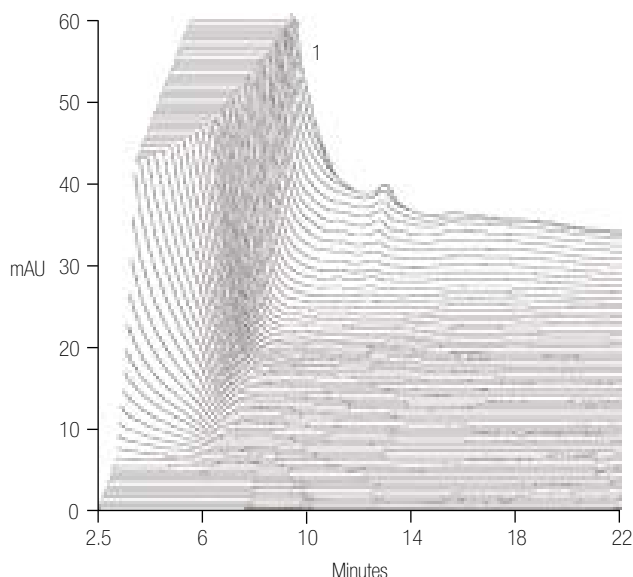|	
Column:	Dionex IonPac NS1 and NG1, 10 µm
Eluent:	0.25% Acetonitrile gradient; 0.25% to 0.5% at 2.5 min to 9% at 18 min in 150 mN sulfuric acid
Flow Rate:	1.0 mL/min
Sample Volume:	500 µL
Detection:	Absorbance, 200–325 nm
Peaks:	1. Copper matrix

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.

Results and discussion

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 onefifth 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.
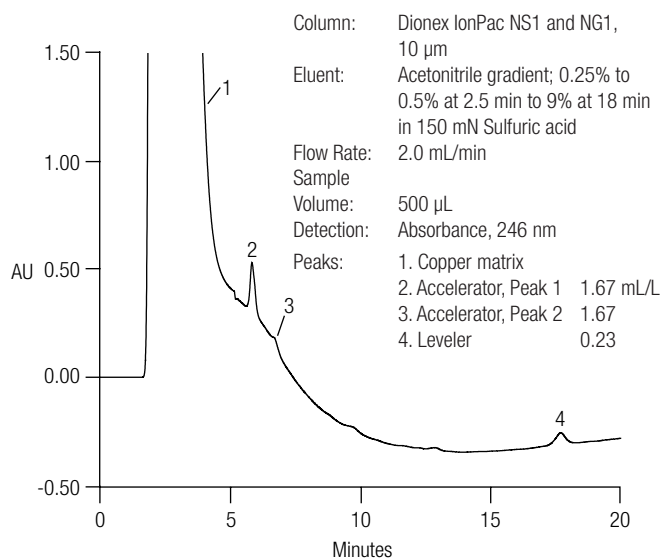
To verify proper quantification of the additives, increasing concentrations of the Accelerator and Leveler were spiked into the acid copper makeup solution. Three replicate injections were made at each calibration level. Spikes of 1.67, 4.2, and 11.1 mL/L for the Accelerator and 0.23, 0.57, and 1.52 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.

Column: Dionex IonPac NS1 and NG1, 10 µm
Eluent: Acetonitrile gradient; 0.25% to 0.5% at 2.5 min to 9% at 18 min in 150 mN Sulfuric acid
Flow Rate: 2.0 mL/min
Sample Volume: 500 µL
Detection: Absorbance, 246 nm
Peaks: 1. Copper matrix
2. Accelerator, Peak 1   1.67 mL/L
3. Accelerator, Peak 2   1.67
4. Leveler   0.23

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

Column: Dionex IonPac NS1 and NG1, 10 μm
Eluent: Acetonitrile gradient; 0.25% to 0.5% at 2.5 min to 9% at 18 min in 150 mN sulfuric acid
Flow Rate: 2.0 mL/min

Sample Volume: 500 μL
Detection: UV/PDA 200-325 nm
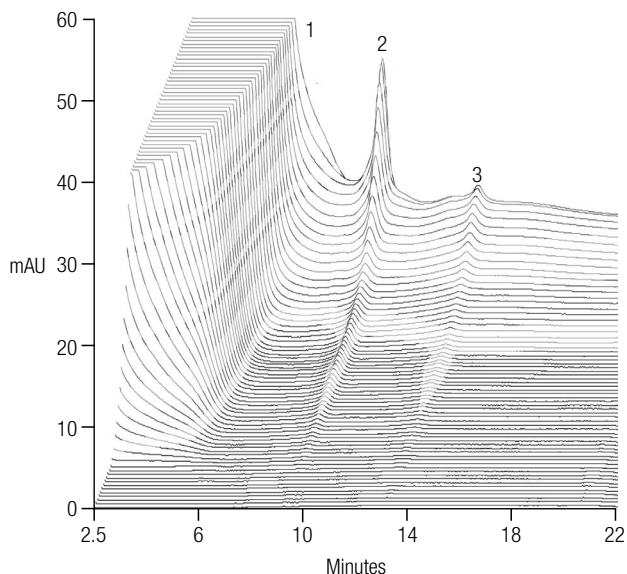Peaks: 1. Copper matrix
2. Accelerator, Peak 1
3. Accelerator, Peak 2

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

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.
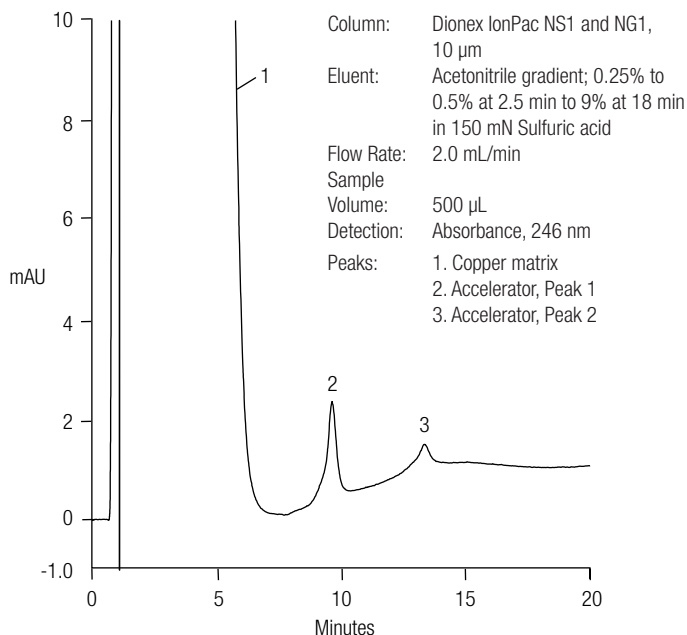
Column: Dionex IonPac NS1 and NG1, 10 μm
Eluent: Acetonitrile gradient; 0.25% to 0.5% at 2.5 min to 9% at 18 min in 150 mN Sulfuric acid
Flow Rate: 2.0 mL/min
Sample Volume: 500 μL
Detection: Absorbance, 246 nm
Peaks: 1. Copper matrix
2. Accelerator, Peak 1
3. Accelerator, Peak 2

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.

Column: Dionex IonPac NS1 and NG1, 10 μm
Eluent: Acetonitrile gradient; 0.25% to 0.5% at 2.5 min to 9% at 18 min in 150 mN sulfuric acid
Flow Rate: 2.0 mL/min

Sample Volume: 10 μL
Detection: UV/PDA 200-325 nm
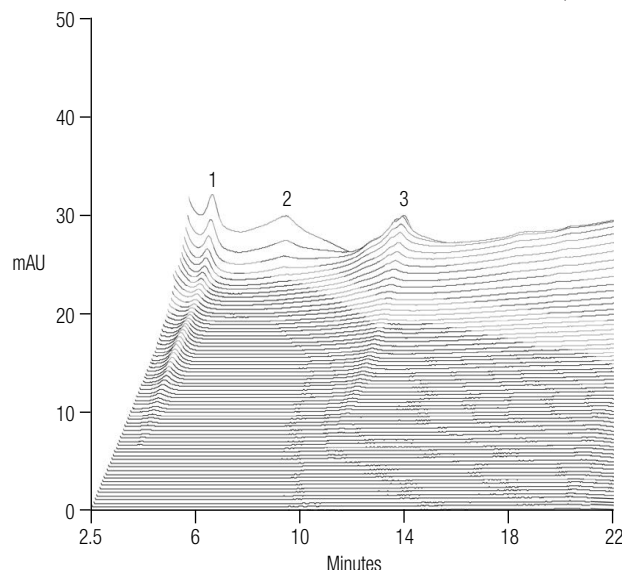Peaks: 1. Byproduct A
2. Byproduct B
3. Accelerator, Peak 1

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.

Column: Dionex IonPac NS1 and NG1,
10 µm
Eluent: Acetonitrile gradient; 0.25% to
0.5% at 2.5 min to 9% at 18 min
in 150 mN sulfuric acid
Flow Rate: 2.0 mL/min

Sample
Volume: 10 µL
Detection: UV/PDA 200-325 nm
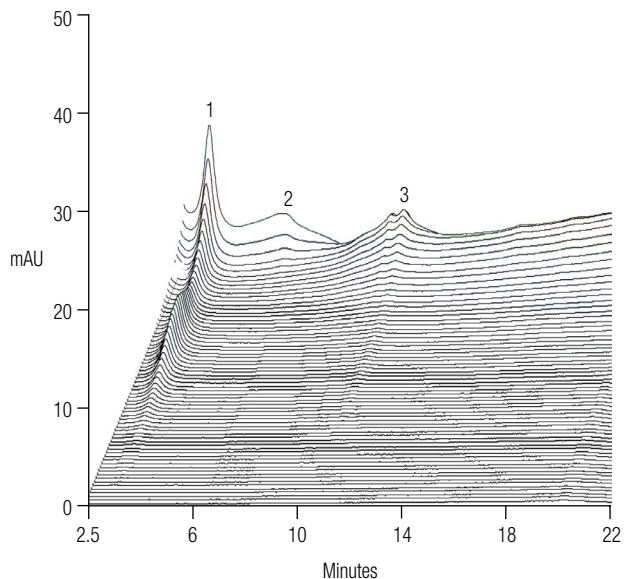Peaks: 1. Spike Byproduct A
2. Byproduct B
3. Accelerator, Peak 1

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

Column: Dionex IonPac NS1 and NG1,
10 µm
Eluent: Acetonitrile gradient; 0.25% to
0.5% at 2.5 min to 9% at 18 min
in 150 mN sulfuric acid
Flow Rate: 2.0 mL/min

Sample
Volume: 10 µL
Detection: UV/PDA 200-325 nm
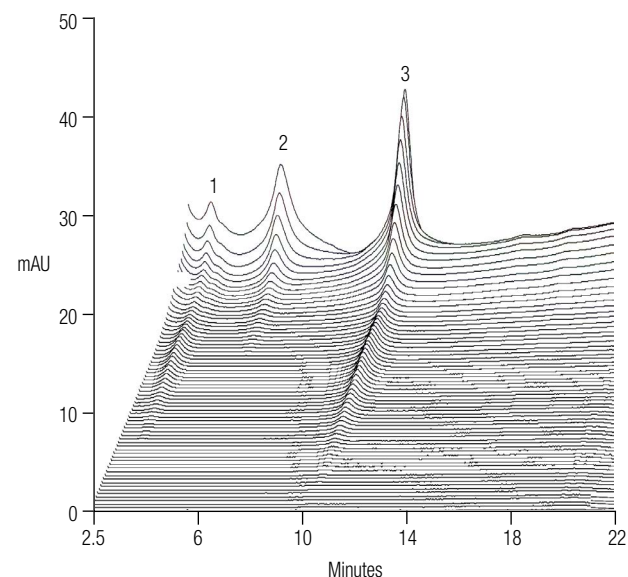Peaks: 1. Byproduct A
2. Byproduct B
3. Accelerator, Peak 1

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

Precautions

It is essential that the Dionex IonPac 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 Dionex AS40 autosampler should not be used for this application due to the highly acidic nature of the samples.

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