Quantitation and Characterization of Copper Plating Bath Additives by Liquid Chromatography with Charged Aerosol Detection

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Overview

Purpose: Analytical methods to determine quantities of copper plating bath additives are described. These methods must be stable, sufficiently sensitive, and retain flexibility for use with the many formulations of copper plating baths that exist.

Methods: Two HPLC methods are run simultaneou™sly to quantitatively measure the three additives that are typically used in copper plating baths. Both methods use reversed-phase high pressure liquid chromatography (RP-HPLC), which can be run simultaneously on the Thermo Scientific™ Dionex™ UltiMate™ 3000 HPLC. The accelerator and suppressor are measured using the Thermo Scientific™ Dionex™ Corona™ charged aerosol detector; the accelerator and leveller are measured using the Thermo Scientific™ Dionex™ Coulochem™ III electrochemical detector (ECD).

Results: The methods are precise and sensitive for the determination of all additives. A quantitative measure of suppressor and suppressor degradation is presented. Calibration curves and sample analysis results are reported for all additives. Both analyses can be run using the same sample preparation.

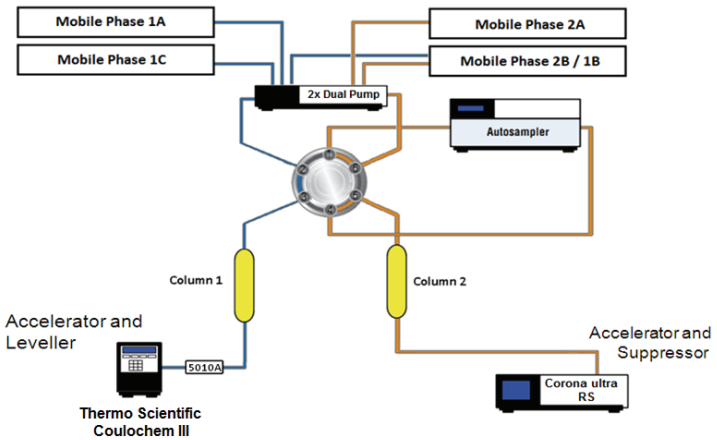
Introduction

Copper plating baths are used in the manufacture of a multitude of products, from the relatively humble cooking pot to the most advanced integrated circuits and satellites. In order to provide the highest quality and most consistent products with copper plated components, the plating process must be well characterized and tightly controlled.

One of the most common approaches to the copper plating is the acid bath, using copper sulfate, sulfuric acid, and a number of additives, namely the accelerator (typically a bis(sulfoalkyl) disulfude) , suppressor (a polyalkylglycol), and leveller (either a large molecular weight polymer or small molecule containing nitrogen or sulfur). Each modifier serves a particular function controlling the speed of plating, surface wetting, and gap-filling in order to provide a smooth surface. The most commonly used technique, cyclic voltammetric stripping (CVS), measures these additives separately or combined, and has been cited as being slow (hours) and not very accurate.[1] HPLC has also been investigated, but with few published results. The accelerator and leveller, are present in minute concentrations, and a lack of a chromophore for most modifiers limits the choice of detectors that can be used for quantitation. HPLC can provide selective quantitation of these additives, without the use of sulfuric acid mobile phases,[1,2] which cause rapid column deterioration.

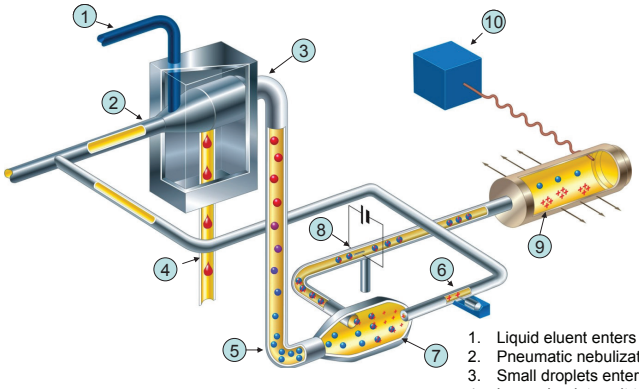
A faster, *quantitative* measure of additives can be achieved using the UltiMate 3000 x2 Dual LC system with two detectors: the Corona ultra RS and the Coulochem III detectors. The Corona charged aerosol detector is a non-selective detector, capable of measuring any nonvolatile analyte at nanogram sensitivities regardless of whether the analyte possesses a chromophore or not. The Coulochem III detector is both extremely sensitive and selective and is ideal for measuring low levels of electrochemically active analytes in complex matrices. Both methods can be run simultaneously, as shown in the system schematic in Figure 1. With this configuration, the autosampler can be exchanged between the two systems without interrupting flow to either system.

FIGURE 1. Schematic of the parallel setup HPLC solution for the simultaneous operation of both analytical methods: system 1 for the accelerator and leveller by ECD, and system 2 for the accelerator and suppressor by charged aerosol detector.



The charged aerosol detector is a sensitive, mass-based detector, especially well-suited for the determination of any nonvolatile analyte independent of chemical characteristics. As shown in Figure 2, the detector uses nebulization to create aerosol droplets. The mobile phase evaporates in the drying tube, leaving analyte particles, which become charged in the mixing chamber. The charge is then measured by a highly sensitive electrometer, providing reproducible, nanogram-level sensitivity. This technology has greater sensitivity and precision than evaporative light scattering (ELS) and refractive index (RI), and it is simpler and less expensive to operate than a mass spectrometer (MS). Typical characteristics of charged aerosol detection include: low-nanogram on column (o.c.) amounts detected, over four orders of magnitude of dynamic range, and high precision results, typically less than two percent of peak area RSD. Analyte response is also largely independent of chemical structure, providing clear relationships among different analytes in a sample.

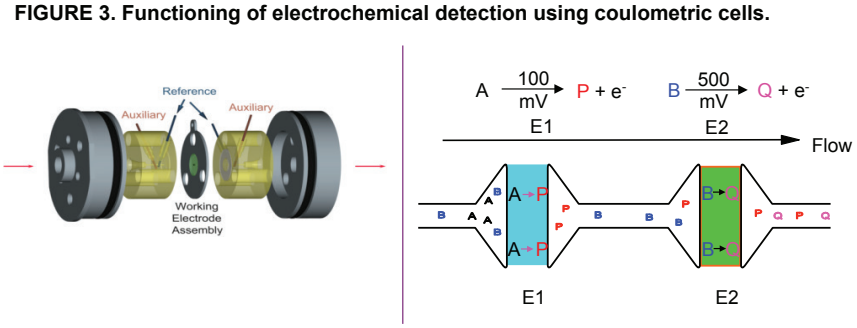
FIGURE 2. Schematic and functioning of charged aerosol detection.



1. Liquid eluent enters from HPLC system
2. Pneumatic nebulization occurs
3. Small droplets enter drying tube
4. Large droplets exit to drain
5. Dried particles enter mixing chamber
6. Gas stream passes over corona needle
7. Charge gas collides with particles and charge is transferred
8. High mobility species are removed
9. Charge measured by electrometer
10. Signal transferred to chromatographic software

The Coulochem III ECD uses unique coulometric working electrodes that offer extreme sensitivity and selectivity, well beyond those achieved by traditional amperometric electrodes. The selectivity of serially placed coulometric electrodes is presented in Figure 3. Typically the first electrode is held at a low potential, the second at a higher potential. As the analytes pass through from one electrode to the other, labile compounds will respond (oxidize) at the first electrode, leaving the second (downstream) electrode free to measure more stable compounds. Electrodes are 100% efficient, which provides the selectivity. In the example below, analyte A oxidizes to P on electrode 1 (E1) held at 100 mV applied potential effectively removing it from further reaction. Analyte B remains unchanged until it encounters electrode two (E2) at 500 mV applied potential. At E2, analyte B oxidizes to Q. This provides a selective means of determining amounts of different analytes.

FIGURE 3. Functioning of electrochemical detection using coulometric cells.



Methods

Sample Preparation

All copper plating bath standard solutions and samples must be properly neutralized prior to injection onto the HPLC system.

Liquid Chromatography

HPLC System: UltiMate 3000 x2 Dual LC, parallel setup solution
Mobile Phase 1A: Water, 2.5 g/L Sodium perchlorate, 2.5 mL/L 10% perchloric acid
Mobile Phase 1B/2B: Methanol
Mobile Phase 1C: Acetonitrile/methanol (900:100) with perchlorates as above
Mobile Phase 2A: (70% Ethyl amine)/acetic acid in water (6 mL/L:4 mL/L), pH 5-6
Injection Volumes: 100 µL
HPLC Column 1: Thermo Scientific™ Accucore™ C18, 2.6 µm, 4.6 × 150 mm
HPLC Column 2: Thermo Scientific™ **Acclaim**™ 120 C18, 5 µm, 4.6 × 150 mm
Column Temperature: 40 °C
Detector 1: Coulochem III ECD with Thermo Scientific Dionex 5010A Standard Analytical Cell
Electrode 1: +650 mV Electrode 2: +900 mV, relative to Pd
Detector 2: Corona ultra RS Data Rate: 10 Hz Filter: 4
Power Function: 2.00 (5.8 – 8.5 minutes)
Sample Temperature: 20 °C
Analysis Time: 16 minutes
Gradients:

Time (min)	-5	0	1	2	3	5	6	6.1	7	10	10	11
Flow Rate 1 (mL/min)	1.0	0.7		0.7	0.9		0.9	1	1	1.1	1	1.0
%1B	2	2		2	0		0	0	0	2	2	2
%1C	0	0		0	35		40	100	100	0	0	0
Flow Rate 2 (mL/min)	0.7	0.7	0.7	0.75	0.65	0.6	0.55			0.8		0.7
$2B	2	2	2	2	25	55	100			100		2

Data Analysis

The HPLC system, data collection, and processing were all operated by and performed on the Thermo Scientific™ Dionex™ Chromeleon™ 7.1 software.

Results

The samples of plating bath and of plating bath additive stock solutions (“standards”) were from two, unrelated sources. As a result, the components of the plating bath samples may not be the same as those of the standards. Consequently, samples were analyzed according to nominal concentrations (NC) used by the source of the standards, where analytes matched.

Accelerator and Leveller Analysis by Electrochemical Detection

Standards of stock additive solutions were prepared in concentrations of 300% NC, and serially diluted to low concentrations. Analytical runs were made in triplicate to determine calibration curves and instrument precision, shown in Figures 4 and 5, respectively. At 100% NC, five samples were individually prepared and analyzed once each.

The linear correlation coefficients were high with R^2= 0.9987 and 0.9945 for accelerator and leveller, respectively. Peak area percent RSD values ranged from 0.6 to 2.3 for accelerator and 4.9 to 18.6 for leveller, with the higher values at the low concentrations.

FIGURE 4. Calibration curve for accelerator by LC-ECD at +900 mV from 10 – 300% NC.

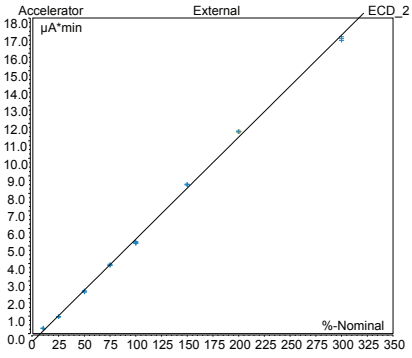


FIGURE 5. Calibration curve for leveller by LC-ECD at +650 mV from 10 – 200% NC.

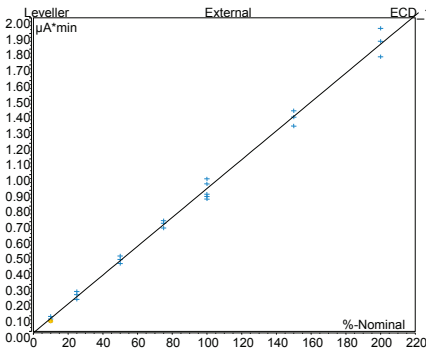
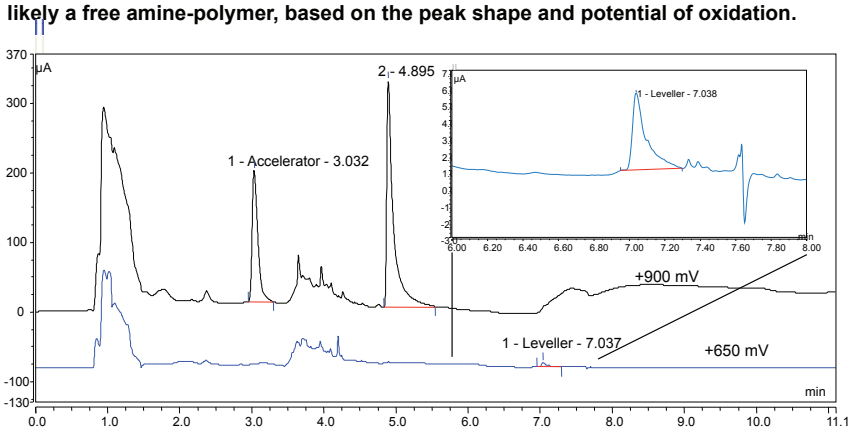


FIGURE 6. HPLC-ECD chromatogram, two potentials overlaid, of used copper plating bath containing accelerator and leveller(s). Peak at 4.895 minutes is likely a free amine-polymer, based on the peak shape and potential of oxidation.



Spike and recovery values were determined for the accelerator and leveller: a bath sample was diluted to 50% to find initial concentrations, and then a second sample was diluted with 100% NC standard, yielding a 50% spike. The overlaid chromatograms are shown in Figure 6. The recovery values were found to be 99% for the accelerator, and 70% for the leveller. This leveller recovery value was confirmed using a second bath sample, and by the method of standard addition, indicating that the recovery value is stable. The signal-to-noise (S/N) value of the leveller (blue) in this spiked sample was 66, indicating that sufficient sensitivity was available for these determinations. Signal-to-noise values of 10 and 3.3 were used to calculate the limits of quantitation (LOQ) and detection (LOD), respectively. The LOQ and LOD values were 1 and 0.3% NC for the accelerator and 20% and 7% NC for the leveller, respectively.

Accelerator and Suppressor Analysis by Charged Aerosol Detection

Standards of stock additive solutions were prepared in concentrations of 300% NC, and diluted to low concentrations. Analytical runs were made in triplicate to determine calibration curves and instrument precision, shown in Figures 7 and 8, respectively. At 100% NC, five samples were individually prepared and analyzed once each. Calibration curves for Corona detectors are non-linear. However, with the use of the Power Function, a linear calibration fit was obtained. This power function adjusts the outgoing signal to provide for linear calibration data, which are important when peak shape changes occur between standard and sample analyte peaks.

The correlation coefficients were high with R^2= 0.9987 and 0.9957 for accelerator and suppressor, respectively. Precision RSD values, based on peak areas varied between 1.0 and 5.3% for the accelerator, and were less than 1% for the suppressor. As with the ECD experiments, the RSD precision values of the sample at 100% NC showed similar values using the charged aerosol detector, indicating that sample preparation is reproducible.

In addition to method accuracy and precision data, the LC-charged aerosol detector method was evaluated for spike recovery in a similar manner as indicated for the ECD evaluation. Recovery values for the accelerator was 103%, and for the suppressor, 95-100%. Analyte resolution was also evaluated. Four peaks were resolved for this accelerator (not shown).

The sensitivity for the accelerator was found to be 3% NC for LOQ, based on a S/N ratio of 10. In the sample chromatograms shown in Figure 9, two plating bath samples are overlaid consisting of a new and a used (diluted 50%) plating bath. The suppressor is seen as the largest peak in the chromatograms, along with many smaller peaks with earlier retention times. These smaller peaks represent lower molecular weight fractions of the suppressor. Compared to the new bath, the suppressor concentrations differed by nearly seven-fold in the used bath, along with a four-fold increase in the relative amounts of the smaller molecular weight fractions. These changes are related to suppressor degradation as the bath is operated.[3] As the plating bath is used, additives are consumed by the process and eventually replenished, as indicated by analytical determinations. For example, the ECD results indicate that the amount of accelerator in the used bath increased by 2.5-fold, relative to the new bath.

FIGURE 7. Inverted calibration curve for accelerator by LC-charged aerosol detector from 0.6-20 mL/L (200% NC)

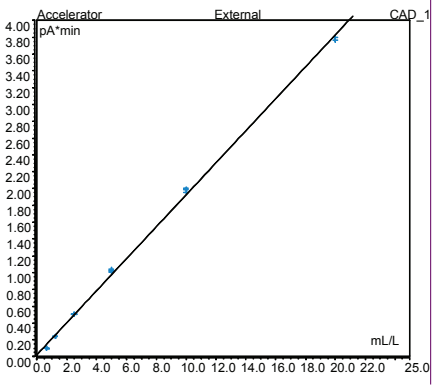


FIGURE 8. Inverted calibration curve for suppressor by LC-charged aerosol detector from 0.6-20 mL/L (200% NC)

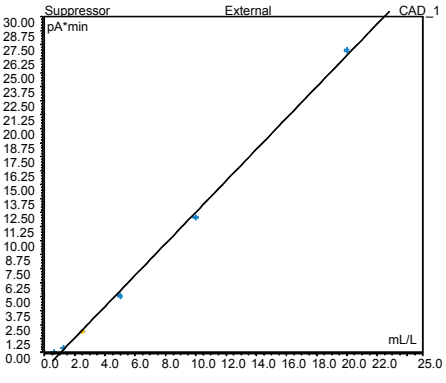
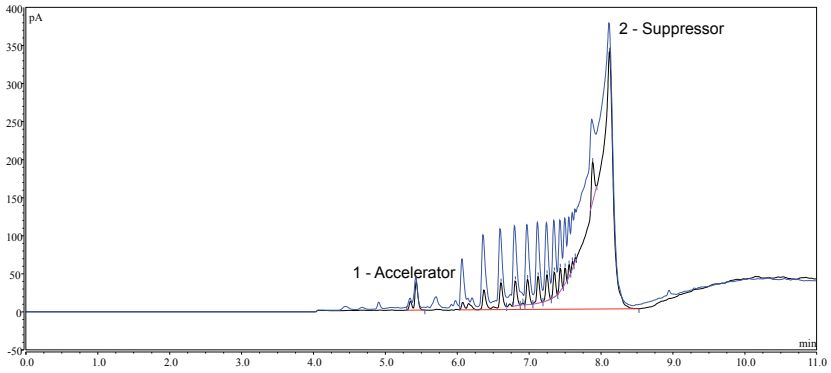


FIGURE 9. Overlay chromatograms of new (in black) and used (in blue, diluted 50%) copper plating baths, using HPLC with charged aerosol detection.



Conclusions

Using charged aerosol detection and electrochemical detection running in parallel on the UltiMate 3000 2x Dual LC provided excellent quantitative data on the three copper plating bath additives

- Analyses have sufficient sensitivity and range to be applicable to many plating bath compositions.
- Analysis was rapid, providing results for neutralized samples in as little as 22 minutes.
- The method is extremely versatile, enabling resolution for different additives of the same class, and can be adjusted to accommodate different bath compositions.
- The assay also resolved a number of potentially important degradants.

References

1. Hong, K. *J. Korean Phy. Soc.*, **43**(2), *2003*, pp. 286-289.
2. Application Note 139: Determination of Additives and Byproducts in an Acid Copper Plating Bath by Liquid Chromatography, LPN1251-01, 2002. Dionex, Part of Thermo Fisher Scientific. http://www.dionex.com/en-us/webdocs/4755-AN139_V16.pdf (accessed 24 Jan 2011).
3. Pavlov, M.; Shalyt, E; Bratin, P. A New Generation of CVS Monitors Cu Damascene Plating Baths. Electro IQ.[Online] http://www.electroiq.com/articles/sst/print/volume-46/issue-3/features/chemical-handling/a-new-generation-of-cvs-monitors-cu-damascene-plating-baths.html (accessed 24 Jan 2012).

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