

Quantitation and Characterization of Copper and Nickel Plating Bath Additives by Liquid Chromatography

Marc Plante, Bruce Bailey, and Ian N. Acworth
Thermo Fisher Scientific, Chelmsford, MA, USA



Overview

Purpose: Analytical methods to determine quantities of copper and nickel 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 simultaneously to quantitatively measure the three additives that are typically used in copper plating baths. Both methods use reversed-phase high-performance liquid chromatography (RP-HPLC), which can be run simultaneously on the Thermo Scientific™ Dionex™ UltiMate™ 3000 HPLC system. The accelerator and suppressor are measured using the Thermo Scientific™ Dionex™ Corona™ Veo™ Charged Aerosol Detector; the leveller and accelerator (again) are measured using the Thermo Scientific Dionex UltiMate 3000 ECD3000RS Electrochemical Detector (ECD). For the nickel plating a method for measuring saccharin and sodium alkyl sulfate (SAS), using ultraviolet absorption (UV) and charged aerosol detection are described.

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.

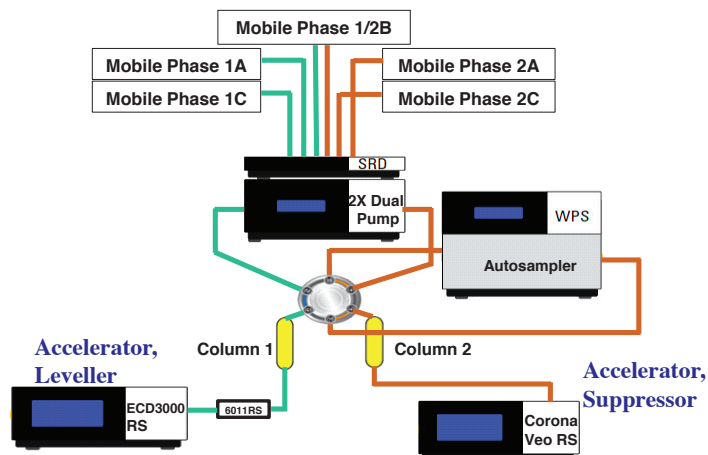
Introduction

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(sodium sulfoalkyl) disulfide), 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 as 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 lack chromophores, which limits the choice of detectors that can be used for quantitation. HPLC can provide selective quantitation of these additives, without the use of corrosive sulfuric acid mobile phases.^{1,2} For nickel additives, saccharin can be measured by UV along with SAS by Corona charged aerosol detectors.

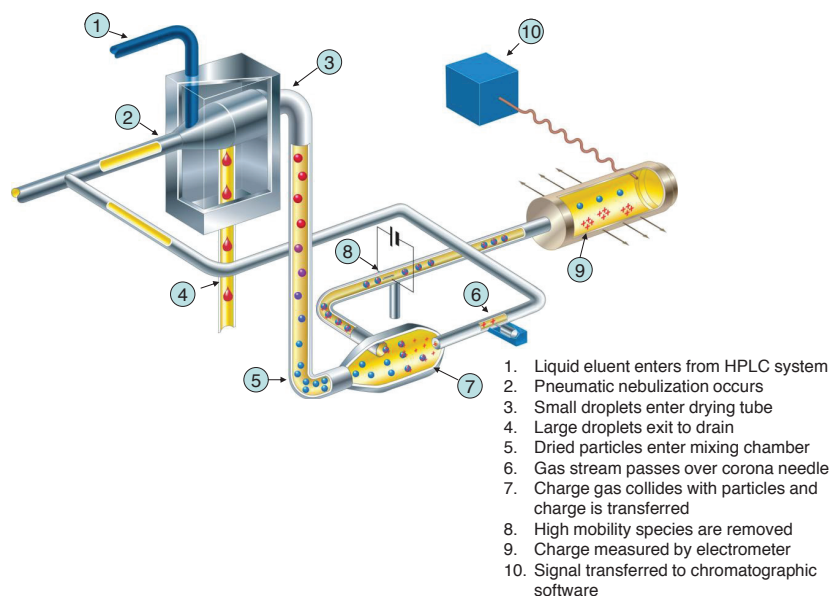
A faster, *quantitative* measure of additives can be achieved using the UltiMate 3000 x2 Dual LC system with two detectors: the Corona Veo RS and the ECD3000RS detectors. The Corona charged aerosol detector is a universal detector, capable of measuring any nonvolatile analyte to nanograms on column. The ECD3000RS detector is both extremely sensitive and selective and is ideal for measuring low levels of electrochemically active (oxidizable) analytes. Both methods can be run simultaneously, as shown in the system schematic in Figure 1.

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.



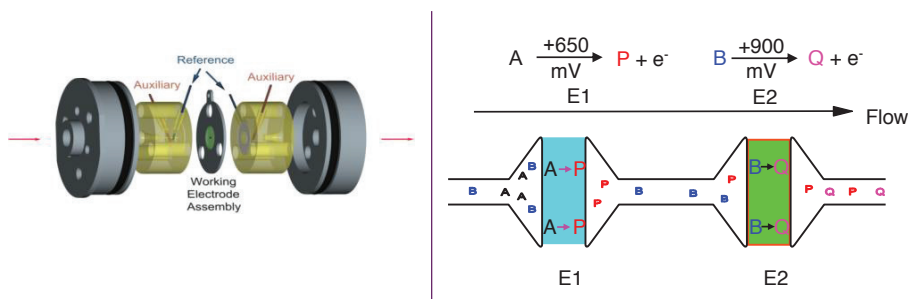
The charged aerosol detector is a sensitive, mass-based detector, especially well-suited for the determination of any nonvolatile analyte independent of chemical characteristics. As shown in Figure 2, the detector uses nebulization to create aerosol droplets. The mobile phase evaporates in the drying 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 linear, dynamic range, and high precision results with typically less than two percent of peak area relative standard deviation (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.



The ECD3000RS 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 +650 mV, relative to palladium, applied potential effectively removing it from further reaction. Analyte B remains unchanged until it encounters electrode two (E2) at +900 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 – Copper Additives

HPLC System: UltiMate 3000 DGP-3000RS system, parallel setup solution
Mobile Phase 1A:* Water, 0.1 v/v-% trifluoroacetic acid
Mobile Phase 1B/2B: Methanol
Mobile Phase 1C: * Acetonitrile/methanol (900:100), 0.1 v/v-% trifluoroacetic acid
Mobile Phase 2A: (70% Ethyl amine)/acetic acid in water (6 mL/L:4 mL/L), pH 5-6
Injection Volumes: 100 μ L
HPLC Column 1: Thermo Scientific™ Accucore™ C18, 2.6 μ m, 4.6 \times 150 mm
HPLC Column 2: Thermo Scientific™ Acclaim™ 120 C18, 5 μ m, 4.6 \times 150 mm
Column Temperature: 40 °C
Detector 1: ECD3000RS with Thermo Scientific Dionex 6011RS Standard Analytical Cell
Electrode 1: +650 mV Electrode 2: +900 mV, relative to Pd
Detector 2: Corona Veo RS Data Rate: 10 Hz Filter: 3.6s
Evaporation Temperature: 50 °C
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

Liquid Chromatography – Nickel Additives

HPLC System: UltiMate 3000 SD or RS system.
Column: Accucore C18, 2.6 μ m, 4.6 \times 150 mm
Mobile phase A: Water, 25 mM diethylamine acetate, pH 5.0
Mobile phase B: Acetonitrile
Flow Rate: 1 mL/min
Column Temperature: 40 °C
Detector 1: DAD-3400RS at wavelength 230 nm
Detector 2: Corona Veo RS, placed after DAD
Data Rate: 10 Hz Filter: 3.6 s
Evaporation Temperature: 25 °C
Power Function: 1.0
Gradient: -5 min, 2 %B; 0 min, 2 %B; 15 min, 95 %B; 20 min, 95 %B; 20 min, 2 %B

Data Analysis

The HPLC system, data collection, and processing were all operated by and performed on the Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System 7.2 SR1 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.

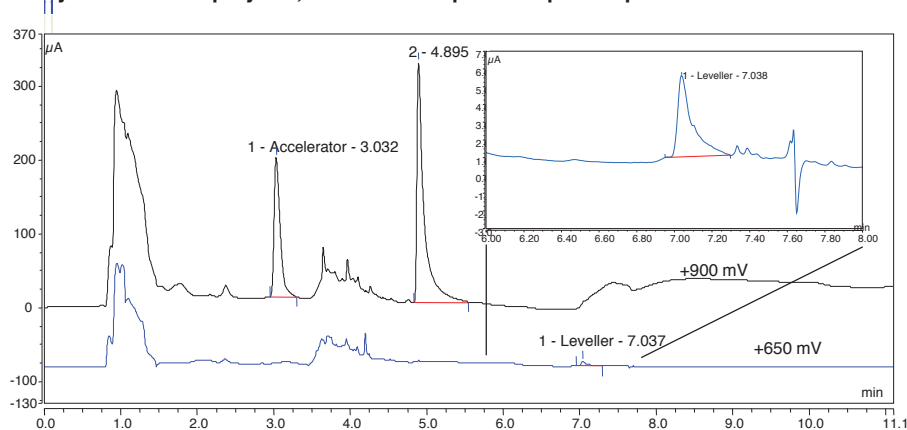
Copper Accelerator and Leveller Analysis by Electrochemical Detection

Standards of stock additive solutions were prepared in concentrations of 300% NC, and serially diluted to low concentrations. Calibration standards were injected in triplicate to determine calibration curves and instrument precision.

The linear correlation coefficients for both additives 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.

A samples was neutralized and analyzed, and the HPLC-ECD chromatograms are shown in Figure 4, with the +650 mV chromatogram in black, and the +900 mV chromatogram shown in blue.

FIGURE 4. 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.



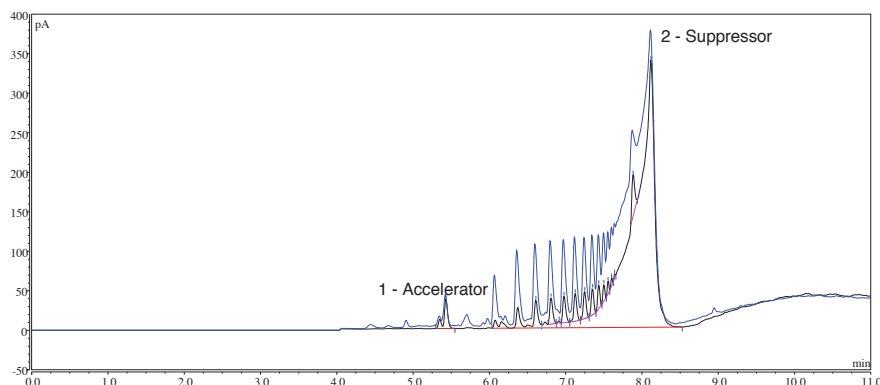
Spike and recovery values, at 50% spike amounts, were determined for the accelerator and leveller: a bath sample was diluted to 50% to find initial concentrations, and then a second sample was diluted with 100% NC standard, yielding a 50% spike. The recovery values were found to be 99% for the accelerator, and 70% for the leveller. 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.

Copper Suppressor Analysis by Charged Aerosol Detection

Standards of stock additive solutions were prepared in concentrations of 300% NC, and diluted to low concentrations. Calibration standards were injected in triplicate to determine correlation and precision. The linear calibration correlation coefficients were $R^2=0.9987$ 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. In addition to method accuracy and precision data, the LC-Charged Aerosol Detection 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%.

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 5, 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 Both accelerator and suppressor can be determined as well as bath quality, as a measure of relative suppressor degradation.

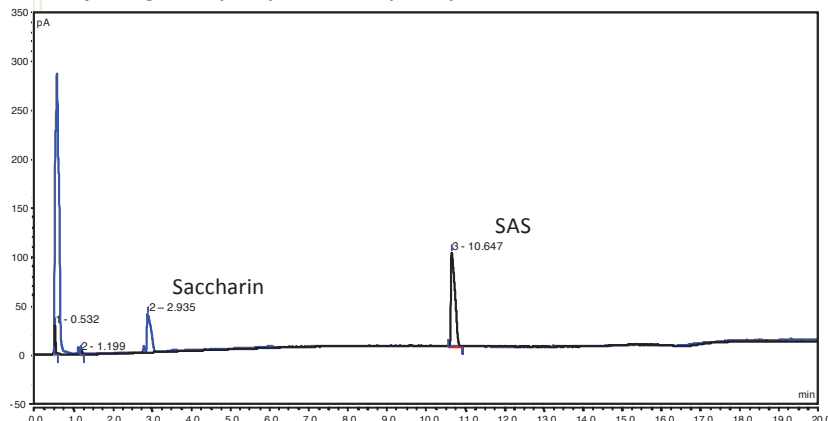
FIGURE 5. Overlay chromatograms of new (in black) and used (in blue, diluted 50%) copper plating baths, using HPLC with charged aerosol detection.



Nickel Saccharin and SAS Analysis by HPLC–UV–Charged Aerosol Detection

A nickel plating bath matrix sample was spiked with an amount of saccharin and analyzed using the conditions outlined above. Clear retention of the analytes was evident, by HPLC-Charged Aerosol Detection, as shown in Figure 6. Calibration and sample analyses were conducted (not shown), and the results were quantifiable. Also, the use of saccharin for the determination of saccharin-related impurities by HPLC-UV at 230 nm is possible (not shown).

FIGURE 6. HPLC-Charged Aerosol Detection chromatogram of saccharin in nickel plating bath (blue), and SAS (black) overlaid.



Measurement Capability

Gage studies were conducted on analyses of organic additives in plating baths by current metrology and by the HPLC-Charged Aerosol Detection methods. The results, shown in Table 1, demonstrated that the HPLC methods are significantly more capable than previous methods, with SV/T (standard variance relative to process tolerance) values significantly reduced. Methods where the SV/T values < 7 are considered to be highly capable, and those between 10 – 30 need to be evaluated for risks of errors.

Table 1. Gage evaluation comparing previous metrology with HPLC-Charged Aerosol Detection metrology.

Additive	SV/T	
	Previous (method)	HPLC–Charged Aerosol Detection
Cu – Accelerator	44.90 (CVS)	9.69
Cu – Suppressor	79.39 (CVS)	18.97
Ni – Saccharin	10.56 (UV)	5.48
Ni – SAS	None	4.50

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.

- HPLC methods are capable of reliably quantifying organic additives in copper and nickel plating baths, as well as determining plating bath quality.
- Analysis times were short, compared to CVS and other analytical methods.
- The method is extremely versatile, capable of being adapted to a variety of plating bath compositions.

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, now part of Thermo 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).

www.thermofisher.com

©2016 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific Inc. products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

Africa +43 1 333 50 34 0
Australia +61 3 9757 4300
Austria +43 810 282 206
Belgium +32 53 73 42 41
Brazil +55 11 3731 5140
Canada +1 800 530 8447
China 800 810 5118 (free call domestic)
400 650 5118

Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland +358 9 3291 0200
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9494
Italy +39 02 950 591

Japan +81 6 6885 1213
Korea +82 2 3420 8600
Latin America +1 561 688 8700
Middle East +43 1 333 50 34 0
Netherlands +31 76 579 55 55
New Zealand +64 9 980 6700
Norway +46 8 556 468 00

Russia/CIS +43 1 333 50 34 0
Singapore +65 6289 1190
Sweden +46 8 556 468 00
Switzerland +41 61 716 77 00
Taiwan +886 2 8751 6655
UK/Ireland +44 1442 233555
USA +1 800 532 4752

Thermo
S C I E N T I F I C

A Thermo Fisher Scientific Brand