

CVS Control of Via Fill Acid Copper Electroplating Baths

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Abstract: Due to the increasing demands placed on acid copper plating solutions to perform via fill plating of blind micro vias it is critical that the plating additives be monitored precisely. This paper presents electrochemical techniques for analyzing additives commonly used in via fill plating baths. The additives, commonly referred to as suppressor, brightener and leveler, all need to be precisely monitored during the production process in order to achieve optimum via fill. Utilizing cyclic voltametric stripping (CVS), these additive types can be monitored with a single analytical instrument when the proper techniques are employed and the measurement procedures are optimized for each additive.

Background: Via fill plating solutions are designed to fill a blind micro via or through hole completely with plated copper metal with a minimum of plating thickness on the surface of the printed circuit board (PCB). Blind micro vias of 75 μm width and 75 μm depth can be via fill plated with about 19 μm of plating thickness on the surface. It is typically required that the dimple in the deposit over the via be less than 12 μm . However, complete fill with no dimple is desired and achievable with the correct use and control of the additives in the via fill plating bath. Figure 1 shows the most desired outcome.

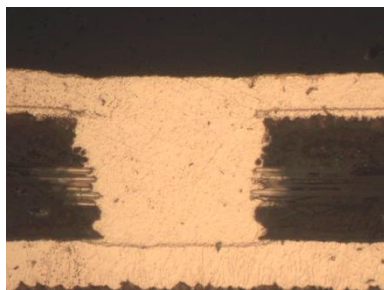


Figure 1 - properly filled via

Many defects in the plated deposit can occur if the additive package is not controlled properly. These defects include; incomplete fill of the via, voids in the deposit in the via, changes in the grain structure of the deposit in the via vs. the surface outside the via, thinning of the deposit at the knee of the via or through holes. Some of these defects are shown in figure 2.

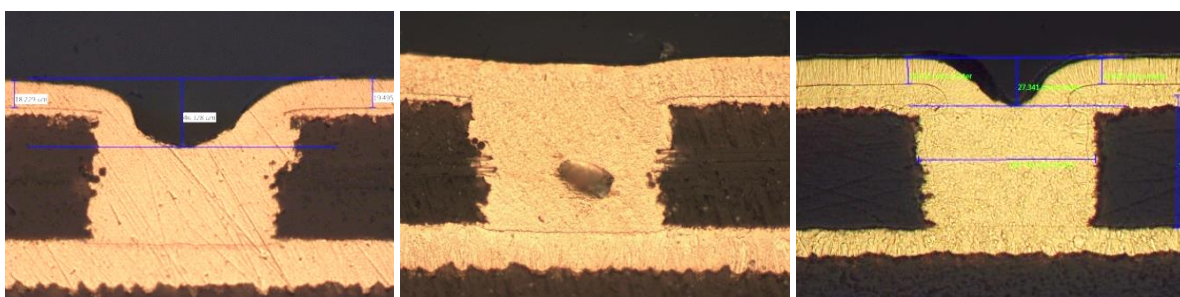


Figure 2 – Defects in via fill plating deposits; a) incomplete fill, b) void in the deposit in the via, c) incomplete fill and columnar deposit on the surface with equiaxial deposit in the via.

These defects can be avoided if cyclic voltametric stripping (CVS) techniques and proper via fill plating additives are employed in the fabrication of PCBs requiring via fill plating. For this paper, CVS analysis was carried out with a production voltammetric measuring analysis system with a production dosing/liquid handling system. Plating of the PCB was performed in a vertical continuous plating (VCP) test cell.

Development of CVS techniques: There are usually three main additive categories in a via fill acid copper electroplating solution. These are commonly referred to as suppressor, brightener and leveler. The presence of a leveler in the plating bath often causes difficulties in obtaining accurate CVS determinations for both the leveler and brightener components. Therefore new techniques for measuring the leveler component and careful choice of additives are required to properly operate and control via fill plating baths.

Cyclic Voltammetric Stripping is an electrochemical technique used for the measurement of organic additives in plating baths. It is based on the effect that the additives have on the rate of electroplating. Regardless of the specific type of organic additive (brightener, leveler, grain refiner, etc.), its activity is reflected in a change in the plating rate.

The analysis is performed in an electrochemical cell using a three-electrode system, one of which is a platinum rotating disk electrode. During measurement, the potential of the platinum electrode is controlled by the instrument. The potential is scanned at a constant rate back and forth between negative and positive voltage limits. A small amount of metal from the plating bath is alternatively plated onto and stripped off the working electrode as the potential is changed. During the scan, the current at the working electrode is measured as a function of potential.

The activity of the additive will affect the plating rate of the metal onto the electrode. The plating rate is determined by calculating the charge required to strip the metal off the working electrode. The relationship between the stripping charge and the activity of the additives is used to quantitatively measure the additives and their components.

A typical CVS scan for acid copper analysis may proceed from 1.5V to -0.225V and back again to 1.5V (figure 3). During this potential sweep the copper metal will be plated onto the platinum electrode and then stripped off again. The area of the curve under the stripping peak is measured in millicoulombs (mC). Each scan is performed in an equivalent manner and multiple scans are performed to both condition the disk and to allow for averaging of the results from each potential sweep.

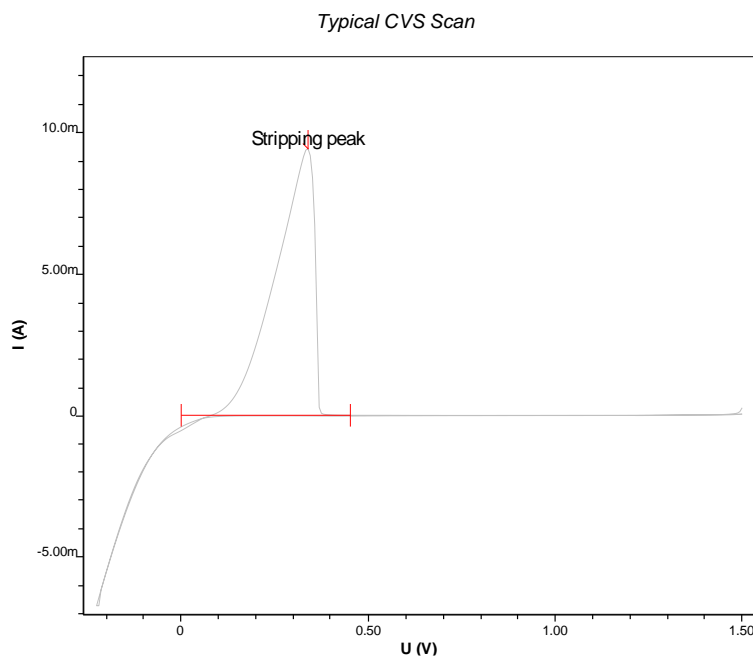


Figure 3 – Typical CVS scan showing the stripping peak. The area under the stripping peak curve is the millicoulomb reading obtained for the scan.

The additives affect the mC reading by changing the overpotential of the plating reaction. The suppressor decreases the mC reading, the brightener increases the mC reading and the leveler decreases the mC reading. All of these additives can be accurately measured by CVS if and only if the proper methods are developed that single out each additives influence on the CVS measurements.

Suppressor Analysis: The suppressor will begin to decrease the mC readings even at very low concentrations. This is shown in figure 4.

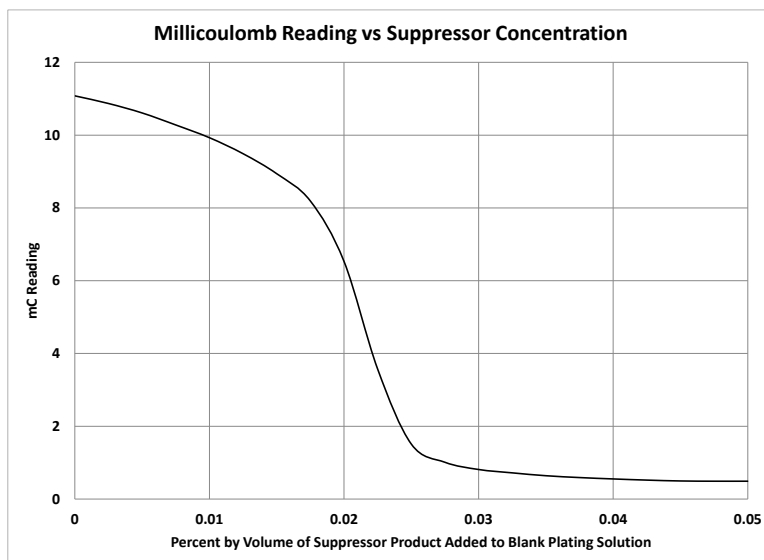


Figure 4 – Effect of adding very small amount of suppressor to a blank plating solution.

Upon adding more suppressor eventually the mC readings will asymptote to a low mC value. Typically the suppressor is contained at a concentration far above the concentration required to asymptote the mC value. Therefore the suppressor's concentration is measured by adding small amounts of the plating bath containing suppressor to a blank solution of plating bath. With each addition of the suppressor containing plating bath the mC reading drops. An arbitrary endpoint is selected, usually about $\frac{1}{2}$ the original mC reading. If, for example, the initial mC reading of the blank bath is 10 mC, then plating bath containing suppressor is added incrementally until the mC reading is below 5 mC. The amount of plating bath added to reach the end point is compared to a standard in order to obtain the suppressor concentration of the plating bath. As stated previously, brightener and leveler can also affect the mC reading. A production bath sample will contain brightener and leveler in addition to suppressor. However, since the suppressor is at a much higher concentration than either the brightener or leveler components, there is little influence from them on the mC reading curve when a production bath is added in small amounts to the blank. An example of a CVS analysis for suppressor in a production bath is depicted in figure 5.

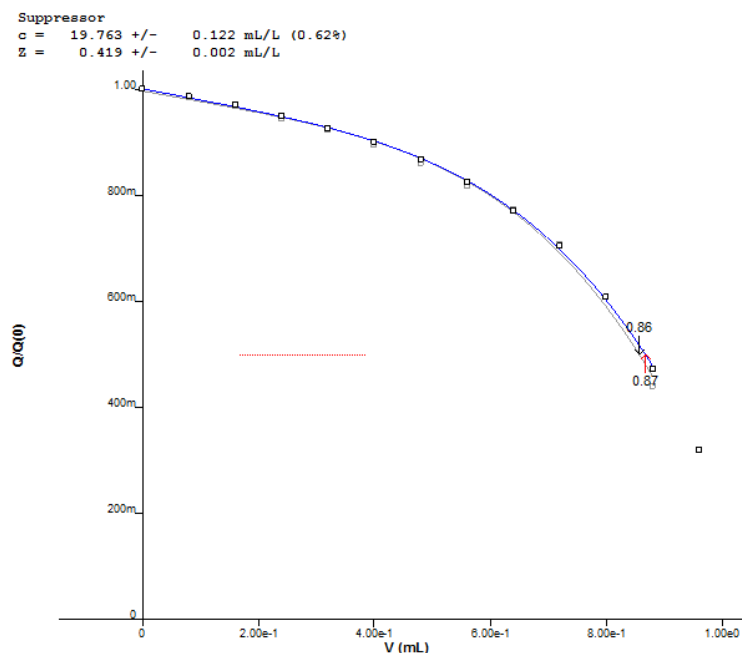


Figure 5 – Suppressor analysis showing the standard curve and the sample curve overlaid (analyzed as 19.763mL/L suppressor). The red line denotes the arbitrary endpoint of 0.5x the initial mC reading of the blank (initial mC readings are normalized to 1.00).

Brightener analysis: There are two primary methods used to measure the brightener in CVS equipment available today. The first measures a blank solution that contains the normal amount of suppressor in order to obtain the intercept value (the mC reading of a bath with no brightener). This solution is then discarded and the bath sample mC reading is measured. A known quantity of brightener is added to perform a method of addition analysis to this separate sample. The intercept value from the suppressor only solution is used to back calculate the brightener concentration in the method of addition. In another more preferred method, first a blank solution that contains the normal amount of suppressor is measured as before; however, the plating bath sample is then added on top of this solution at a fixed ratio. This solution is measured and a known quantity of brightener is added in a method of addition. The CVS unit uses the intercept value of the suppressor only solution, the dilution factor, and the method of addition to properly back calculate the brightener concentration of the bath sample.

A common problem in the brightener determination is that the intercept solution, which represents a production bath with no brightener added, has not been electrolyzed, nor does it contain any of the contaminants or breakdown products in it that the production bath may contain. Therefore, it may not be a good representation of a production bath at a zero concentration of brightener. This causes an error in the brightener analysis. The preferred method stated above helps to minimize this error by using the intercept solution as a blank starting point for the analysis. The lower the ratio of production bath added to the sample the more accurate the intercept value obtained will be. However this must be weighed against the ability of the method to measure low brightener concentrations of a diluted production bath sample. Therefore the proper dilution amount will depend on the brightener level utilized in the production bath. For via fill plating the brightener level is typically fairly high so larger dilutions are appropriate.

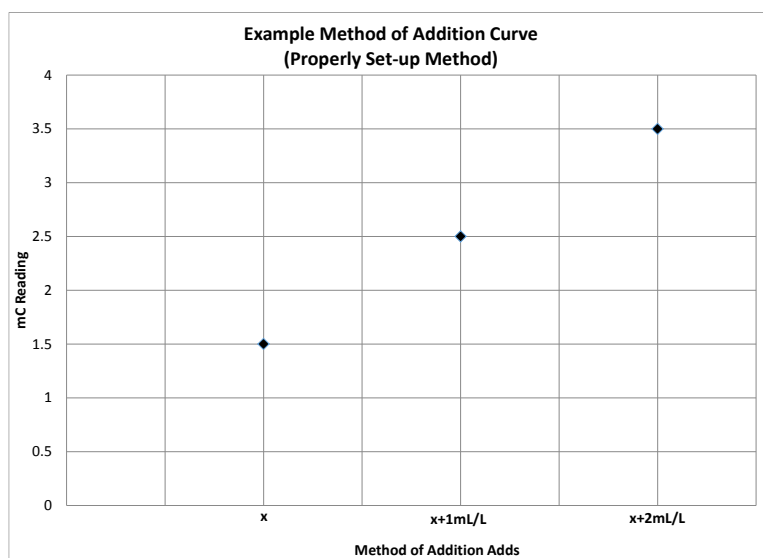


Figure 6 – Example of a brightener analysis utilizing method of addition with a proper set-up.

Let us consider the following example: 30mL of intercept solution gives a reading of 0.5mC. 10 mL of a bath sample is added on top of that to give a total of 40mL. The reading is measured to be 1.5mC as in figure 6. 1mL/L of brightener is added and the reading is measured to be 2.5mC. A second add of 1mL/L is added and the reading is measured to be 3.5mC. The method of addition calculates x to be 1mL/L of brightener based on the slope of the curve and the intercept value. However this solution was diluted to 25% so the actual brightener concentration in the production bath is 4mL/L. If however, the intercept value was 1mC instead of 0.5mC, then x would be calculated as 0.5mL/L in this sample and 2mL/L in the production bath after accounting for the dilution. One can readily see in this example that the correct intercept value is critical to obtaining an accurate brightener concentration. One important factor in optimizing the brightener analysis is to use the proper ranges of the brightener additions and dilution of the sample into the intercept solution so that all the data points are evenly spread as in the example in figure 6. This may need to be done by trial and error.

Another potential problem with brightener method of addition analysis is the possibility of the addition curve to bend down instead of remaining linear as brightener is added. This can be more prevalent in in via fill plating baths than other baths due to the presents of high brightener concentrations and strong levelers found in some via fill plating formulations. Accurate brightener analysis depends on a linear response from brightener additions. Usually if the curve bends down, decreasing the brightener add amounts and diluting the sample more into the intercept solution will solve the problem. However to make sure the response is indeed linear at least three data points need to be taken, the x value and at minimum 2 additions as in figure 6 above.

Leveler Analysis: The authors have developed new methods for analyzing the leveler component of via fill plating baths. Leveler decreases the mC reading. By studying the brightener method of addition curves, it was found that the slope of the brightener method of addition curves changed with different concentrations of leveler in the plating bath. This change in slope can be used to accurately analyze the leveler component independently of the brightener concentration. The method involves making standard solutions of plating baths with varying amounts of leveler added to each standard. To each leveler standard, brightener is added such that a linear curve of brightener concentration vs mC reading is produced. The slope of this line is calculated for each level of the leveler standards as in figure 7. Then, a curve of these slopes vs the leveler concentration is produced as in figure 8. This curve of the leveler concentration vs the slope of brightener additions is compared to the production solution's slope to determine the leveler concentration in a production bath. Since the slope of the curve is all that is required the concentration of the brightener at the start of the analysis does not influence the results.

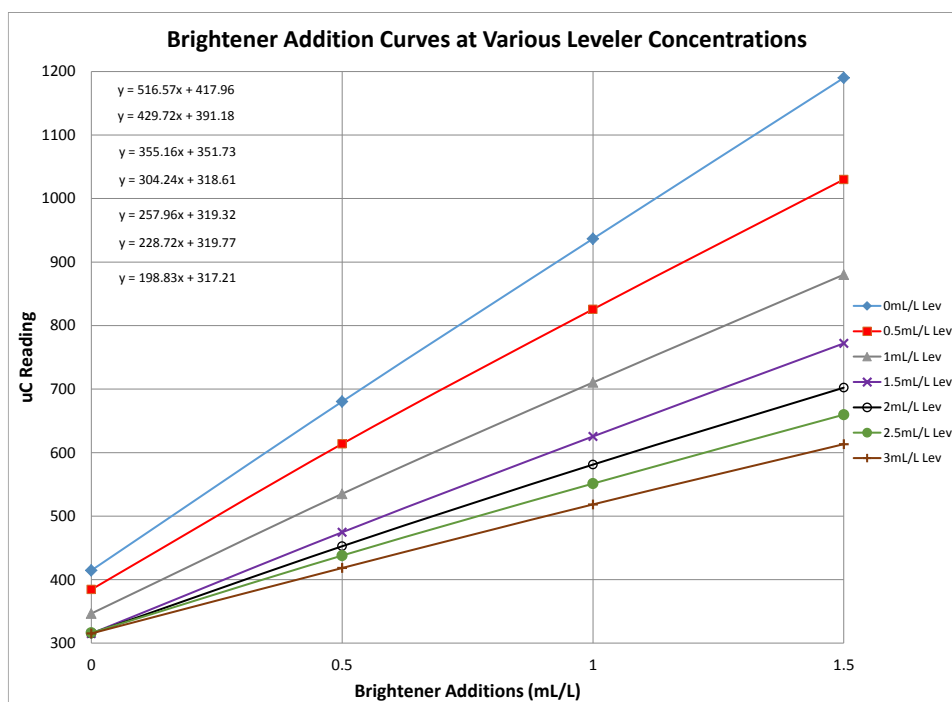


Figure 7 – Brightener addition curves at various leveler concentrations. The equation for each curve is listed in order in the upper left quadrant of the graph.

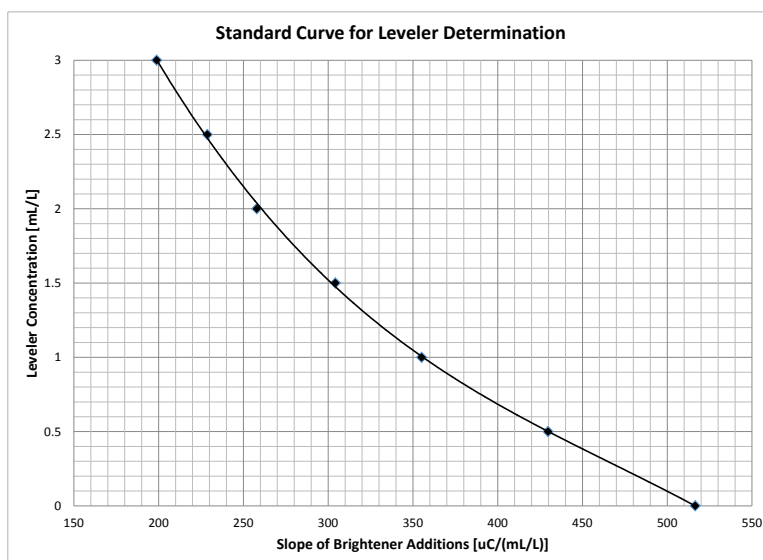


Figure 8 – Standard curve for leveler determination.

Via Fill technology is varied and one leveler type may not be optimum for all technology types. Therefore different types of levelers may be employed for different technologies. Some levelers may cause a more marked change in the brightener addition slope such that at the normal running concentrations the slope is zero or near zero. This requires the sample to be diluted prior to the analysis. For the brightener determination by method of addition in such a system the sample would also require dilution so that the sample responds linearly with a positive slope to brightener additions. In figure 9 another brightener addition curve with various amounts of a stronger leveler is shown.

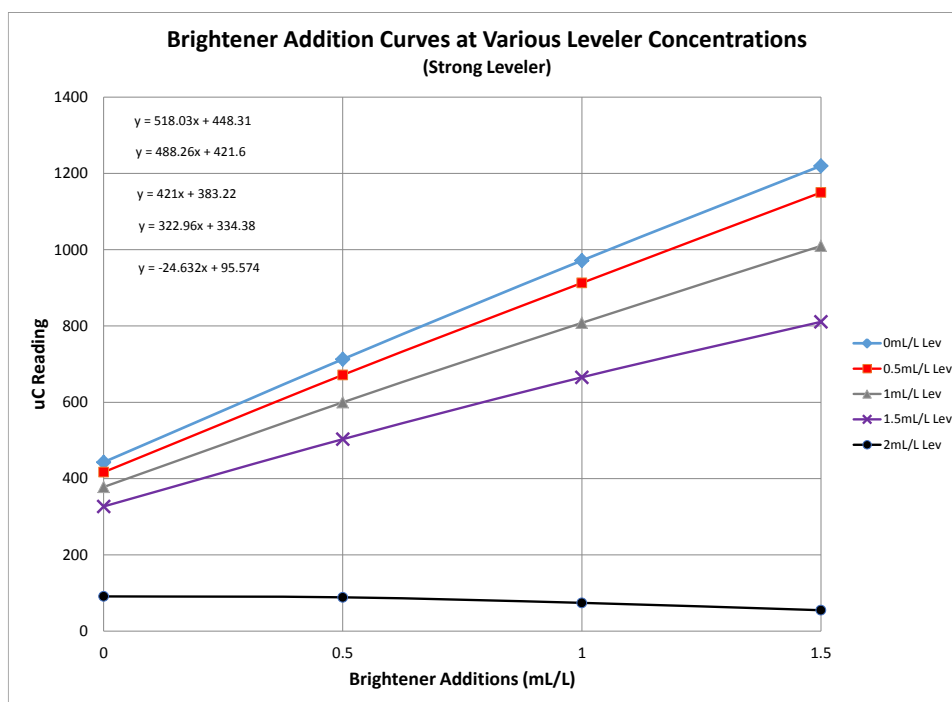


Figure 9 - Brightener addition curves at various leveler concentrations for a strong leveler. The equation for each curve is listed in order in the upper left quadrant of the graph.

As the leveler amount increases, the slope of the brightener additions trends to zero (or negative). For this leveler, if it is employed at greater than 1.5mL/L in the production bath, the sample must be diluted into a plating blank solution that contains the nominal amount of suppressor before analysis.

Figure 10 shows a brightener analysis by method of addition in a plating bath that contains a strong leveler at a high concentration. The strong leveler is not allowing for proper brightener analysis.

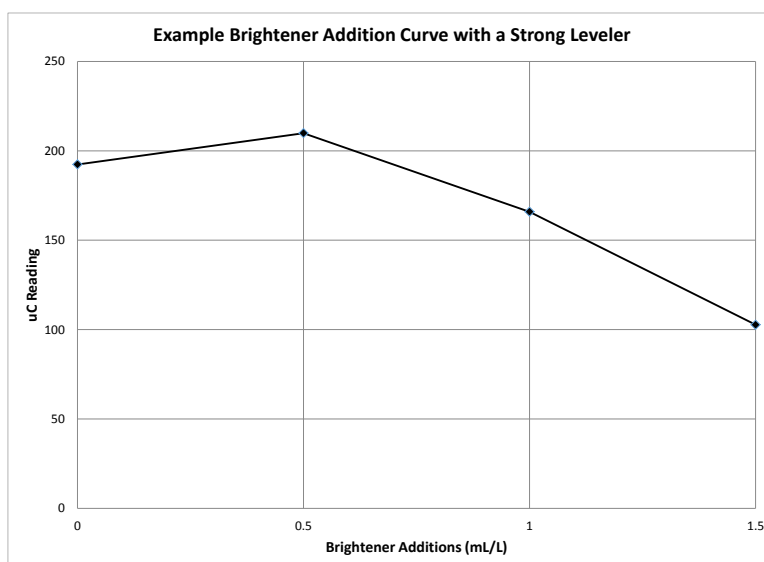


Figure 10 – Example of a brightener addition curve when a strong leveler at high concentrations contained in the bath.

In spite of the fact that brightener is being added the mC value does not increase linearly. This behavior is due to the fact that the leveler adsorbs onto the electrode during the electrolysis of the CVS scan. As the CVS scans proceeds more and more

leveler adsorbs onto the disk from the solution. Eventually the leveler dominates and the mC values decrease with subsequent scans in spite of the fact that brightener is being added.

Strong levelers can influence the next run on the CVS instrument as well. A procedure called conditioning is often performed between plating bath measurements. Conditioning is simply running the CVS scan with a blank solution that contains no additives. A conditioning scan should always give the same result if the CVS instrument, platinum electrode and reference electrode are all working properly and nothing is adsorbed onto the disk that influences the mC readings. For example, a conditioning scan of via fill plating blank with no additives may give a result of about 11mC. In figure 11 below, conditioning was run 8 times after the above attempt to analyze the brightener in a plating bath containing strong leveler at high concentrations. Then the first conditioning solution was discarded and conditioning was repeated with another fresh plating blank solution.

<u>Condition Scan #</u>	<u>mC Reading 1st solution</u>	<u>mC Reading 2nd solution</u>
1	1.96	9.63
2	2.27	9.88
3	2.36	10.12
4	2.28	10.45
5	2.12	10.63
6	2.49	10.79
7	3.03	10.93
8	3.56	10.91

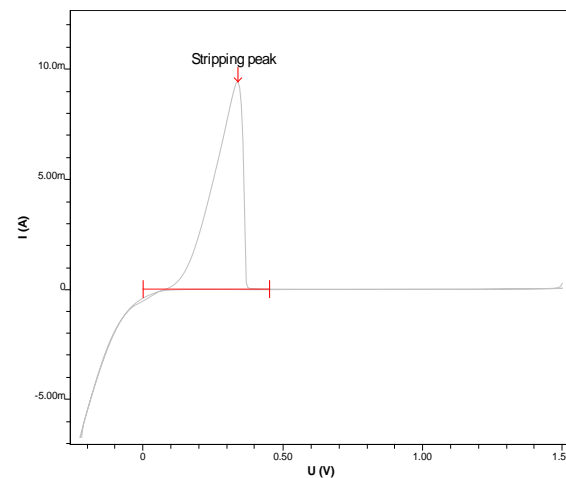
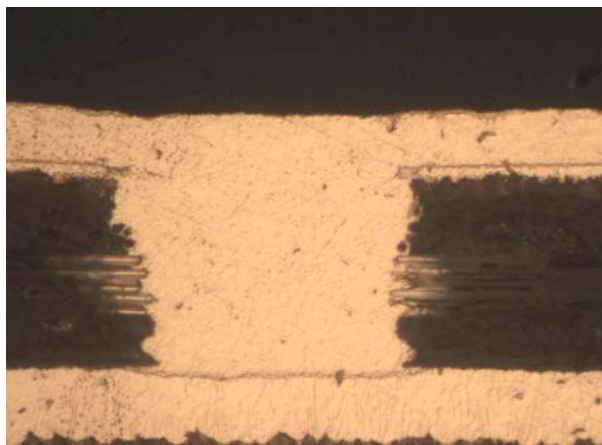
Figure 11 – Effect of a strong leveler on subsequent conditioning scans

Only after discarding the first solution and repeating could the conditioning method give the expected results. This can be a common experience. Often when running the conditioning method after an analysis of via fill plating baths, the first results are very low due to the leveler remaining on the electrode. This problem can be alleviated by diluting all solutions before analysis so that less leveler gets adsorbed onto the disk in the first place. Usually the best procedure for returning the system to a normal state for the next analysis involves first doing the conditioning only a few times and then discarding that solution and repeating the conditioning method a second time. This step is necessary to insure that the system is ready for the next analysis. The conditioning result should be at least 90% of what is considered the historical average for the instrument and blank chemistry before performing any subsequent analysis.

Conclusions: The three primary additives, suppressor, brightener, and leveler, that are commonly contained in via fill plating baths can be independently analyzed by CVS. The suppressor analysis uses only a small amount of plating bath added to a blank solution thus minimizing the influence of the other additives. The optimum procedure for the brightener analysis calls for the plating bath sample to be diluted into a blank solution containing the suppressor rather than running a 100% production bath sample. The production bath dilution and brightener addition amounts need to be carefully set up to give properly spaced data points for the analysis. The authors have created new techniques for measuring the leveler component in via fill plating baths utilizing the slope of brightener additions as the means for determining the leveler concentration independently of the brightener concentration. Some strong levelers can affect the ability to measure the brightener. Levelers that adsorb onto the platinum electrode can influence the results of the next analysis as well. Special care of the instrument and testing the system with a conditioning method to assure results are proper is a necessary step to insure accurate results with CVS analysis.



CVS Control of Via Fill Acid Copper Electroplating Baths

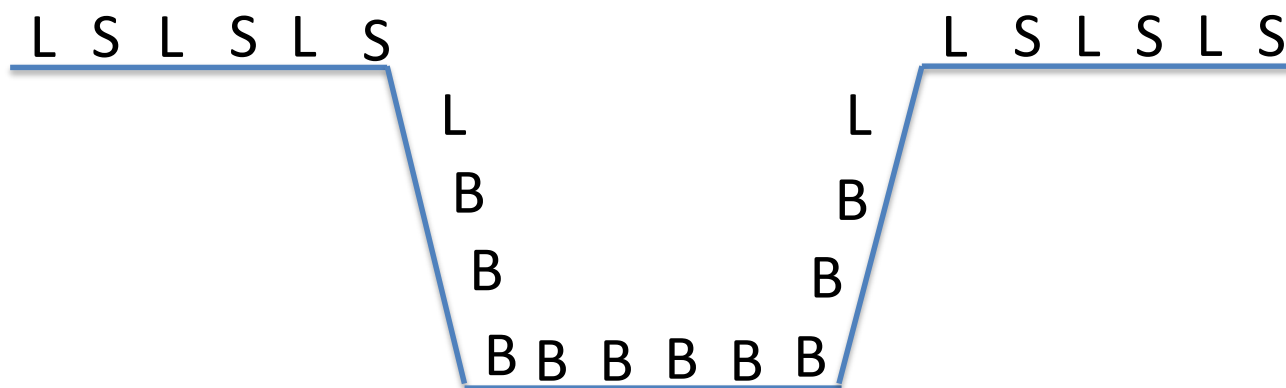


Roger Bernards - OM Group Electronic Chemicals, LLC



Selective Adsorption of Suppressor, Brightener and Leveler

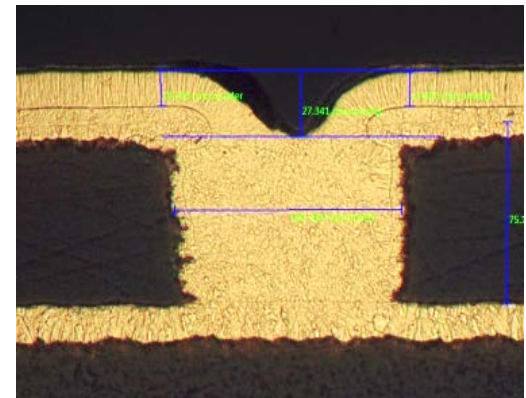
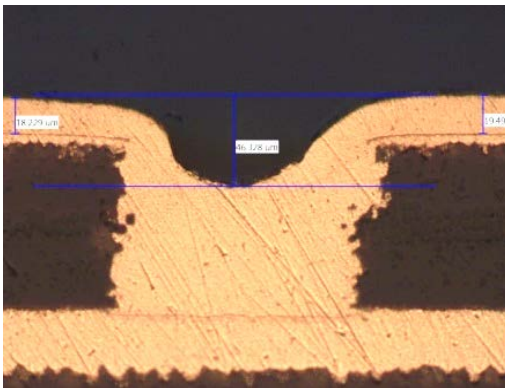
- ❖ Proper filling of micro vias only occurs when brightener selectively adsorbs more preferentially inside the via, and suppressor and leveler adsorbs more preferentially on the surface.
- ❖ The adsorption of these additives is a dynamic process. Additives adsorb and desorb on the surface as the copper plating proceeds and new copper surfaces are constantly being created.
- ❖ Only through precise control of all of the additive concentrations can this preferential adsorption occur properly, therefore CVS control of these additives has become more critical than ever before.





Typical Defects in Via Fill Plating Potentially Stemming from Poor Bath Additive Control

- ❖ Failure to have good fill
- ❖ Thin knees on the through holes
- ❖ Voids in center of the via
- ❖ Columnar plating on surface
- ❖ General changes in grain structure in Via or hole vs. Surface
- ❖ Separation at the bottom of via after solder shock



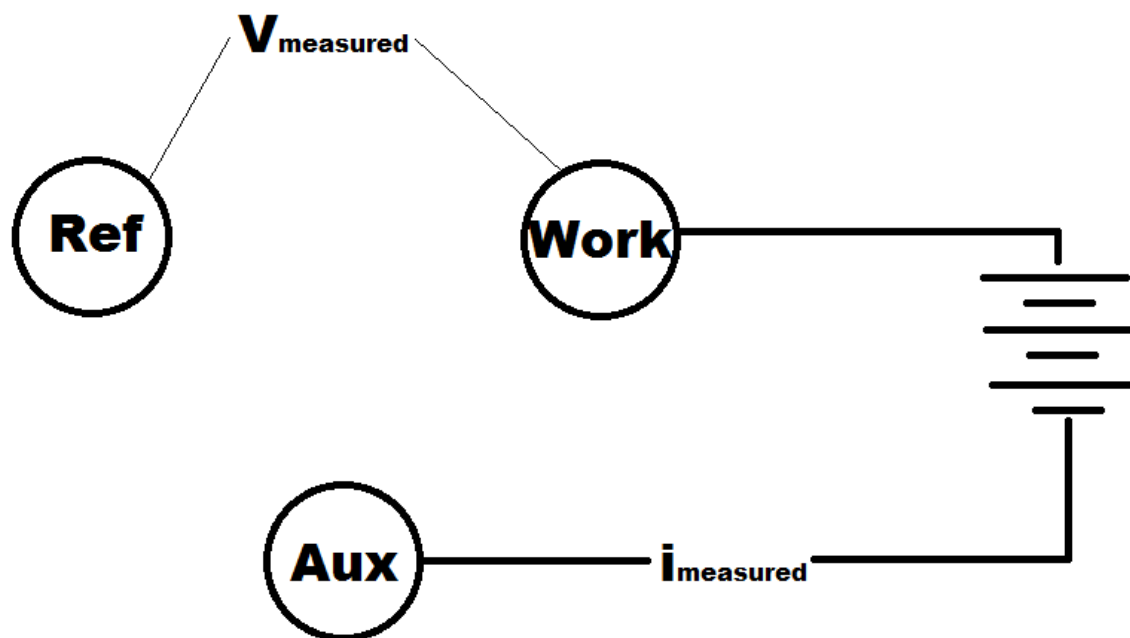


CVS: Cyclic Voltametric Stripping

- ❖ Electrochemical technique that monitors the influence additives have on the current-potential curve of plating baths
- ❖ Indirect measurement of the additive concentration
- ❖ Mature methods for controlling the brightener and suppressor (carrier) components of an acid copper plating bath are established
- ❖ New methods for measuring the leveler component in via fill plating baths have been developed
- ❖ Difficulties obtaining an accurate leveler analysis and difficulties analyzing brightener accurately in formulations containing a strong leveler additive have been common problems for CVS analysis
- ❖ For all additive components, CVS methods need to be carefully optimized to obtain accurate, reproducible results



CVS Utilizes the Three Electrode Cell

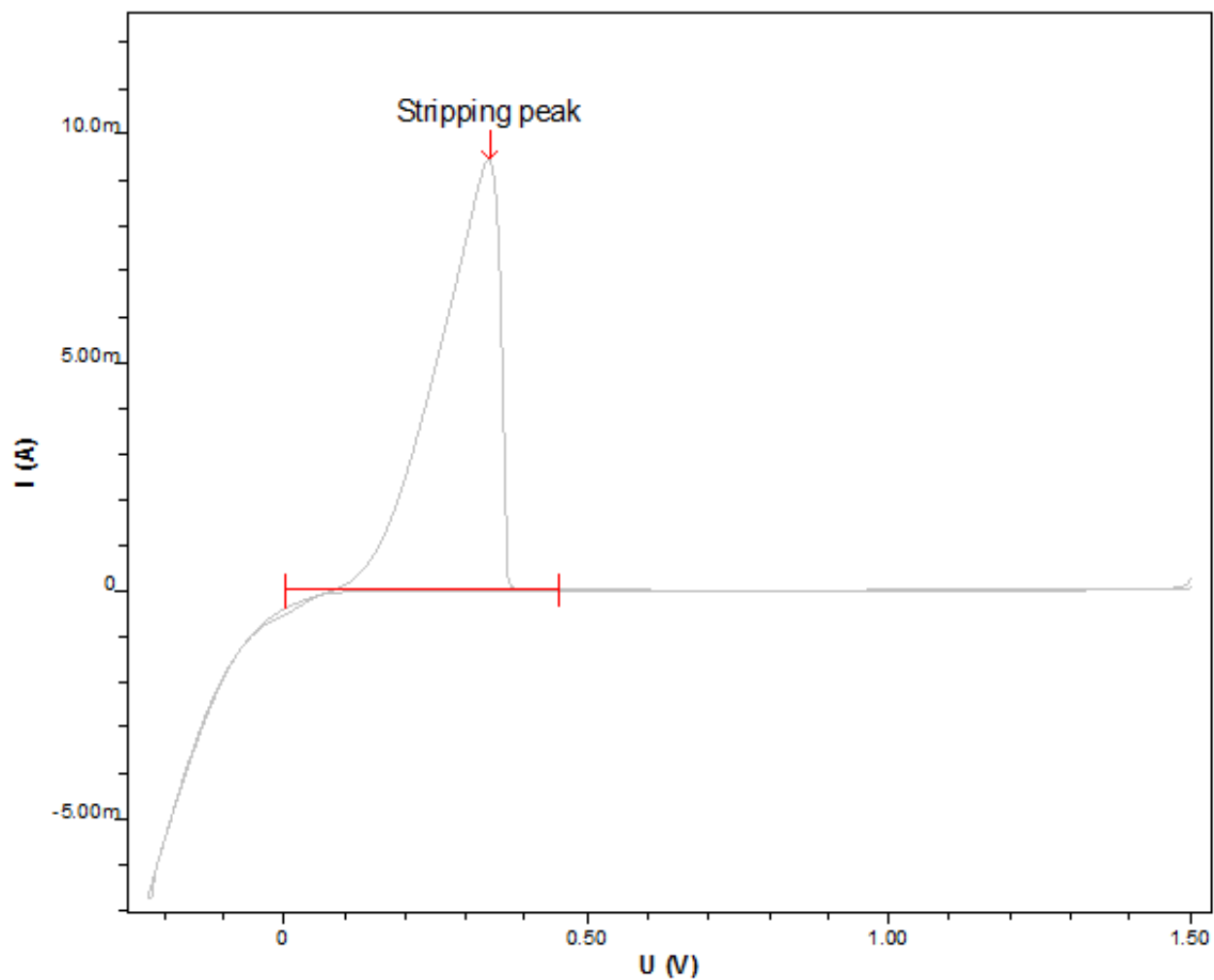


- ❖ The voltage is supplied between the working and auxiliary electrodes.
- ❖ The voltage is measured between the reference electrode and the working Electrode. Virtually no current flows between these electrodes, therefore there is virtually no burden voltage included in the measurement.
- ❖ The current flow occurs between and is measured between the working and auxiliary electrodes.



Typical CVS Scan

Typical CVS Scan



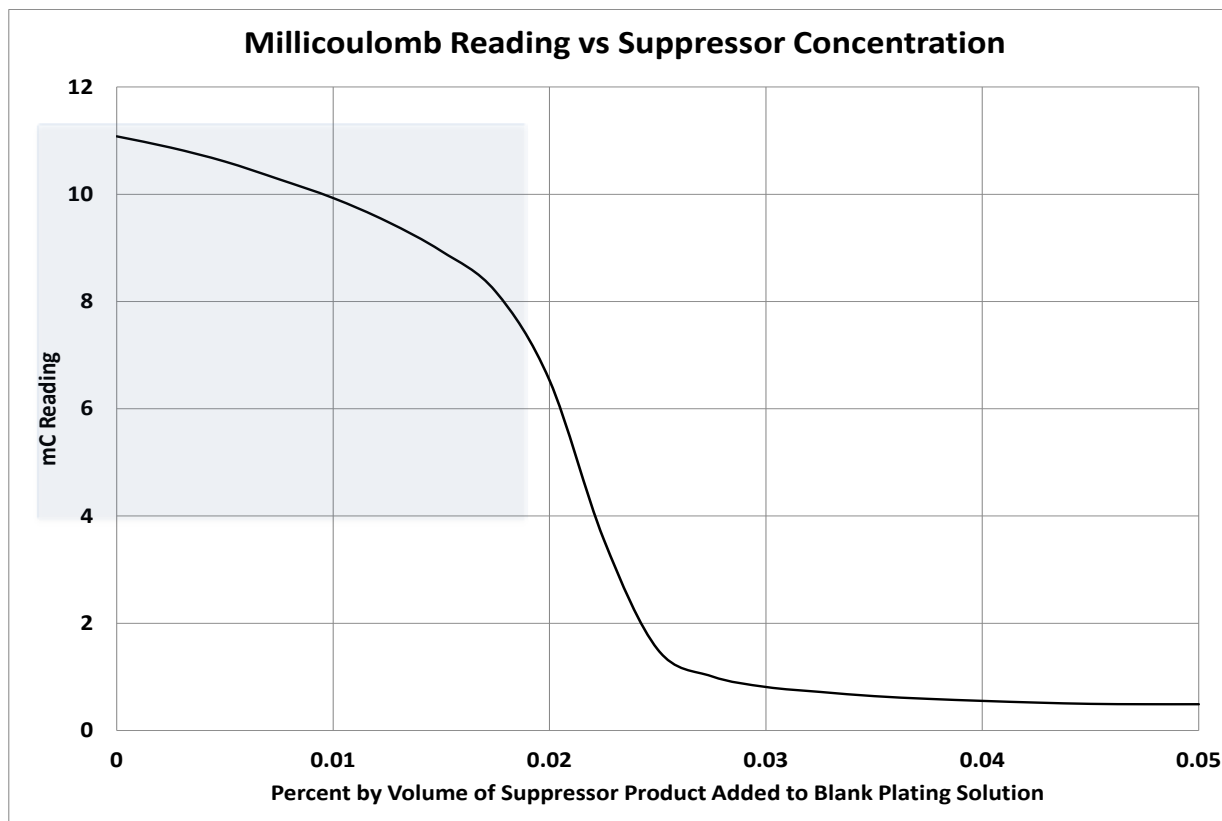


Important Considerations of CVS Experiments

- ❖ The Positive and Negative Vertex Voltages.
- ❖ The Scan Rate.
- ❖ Preconditioning to remove adsorbed species, clean Pt electrode.
- ❖ Reference electrode voltage and care.
- ❖ Millicoulomb reading = Total number of electrons needed to strip the metal off of the working electrode.
- ❖ Charge Transfer Overpotential: The potential difference between the $\frac{1}{2}$ cell's thermodynamically determined potential and the actual potential at which the redox event (plating) is experimentally observed.
- ❖ The complex electrochemical equations that dictate electrochemical behavior (Faraday, Nernst, Cottrell, Tafel, Levich etc) are all derived from Ohms Law:
 $E = IR$.
- ❖ Additives act to change the resistance term in Ohm's Law.



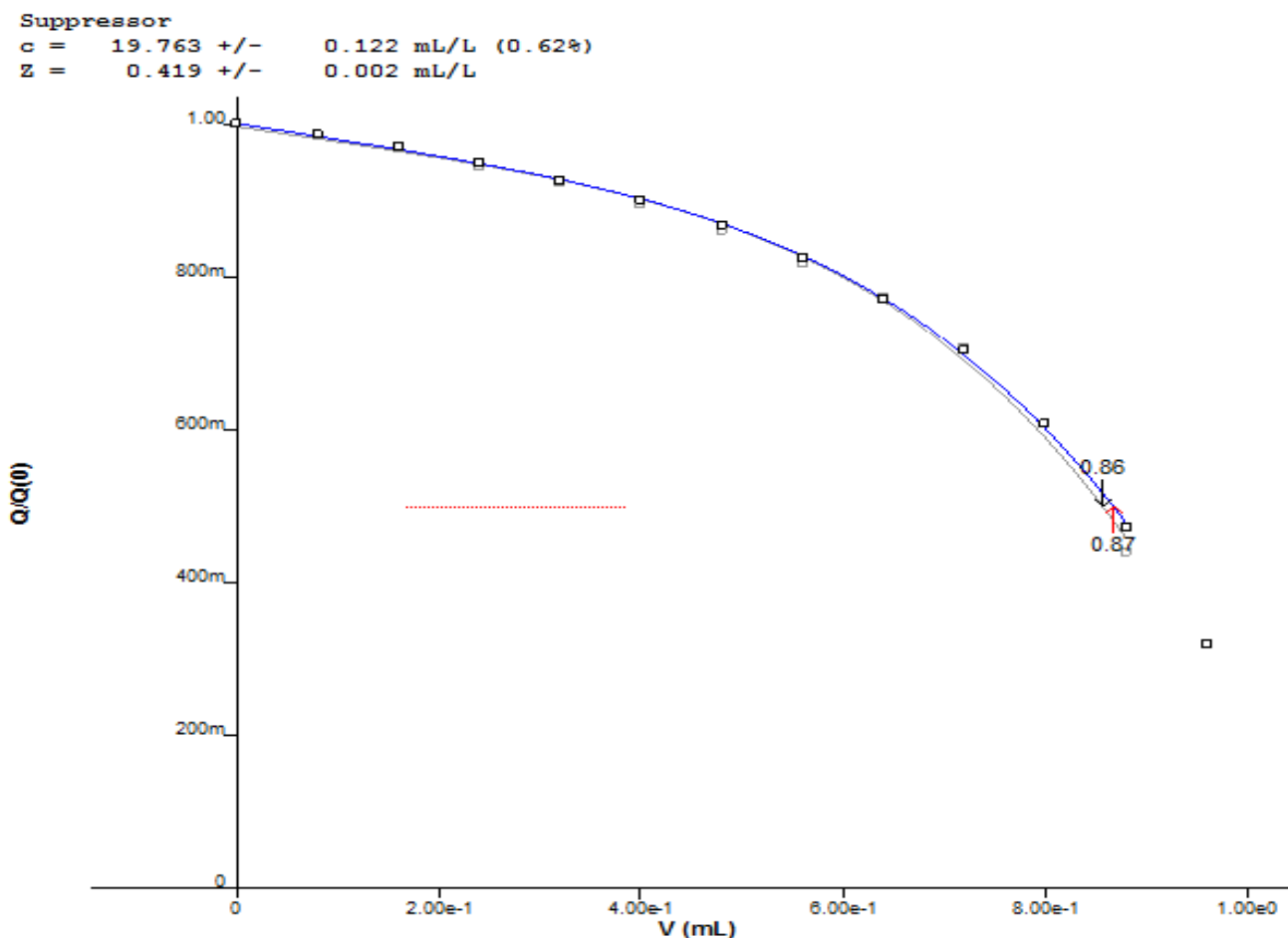
Suppressor Effect on mC Reading



- ❖ Typically the suppressor in the bath is maintained at a concentration far above the level that produces this effect on the mC reading.
- ❖ For this suppressor example the suppressor is maintained at 2%.
- ❖ The analysis is done by adding very small amount of the suppressor containing plating bath solution to a blank solution



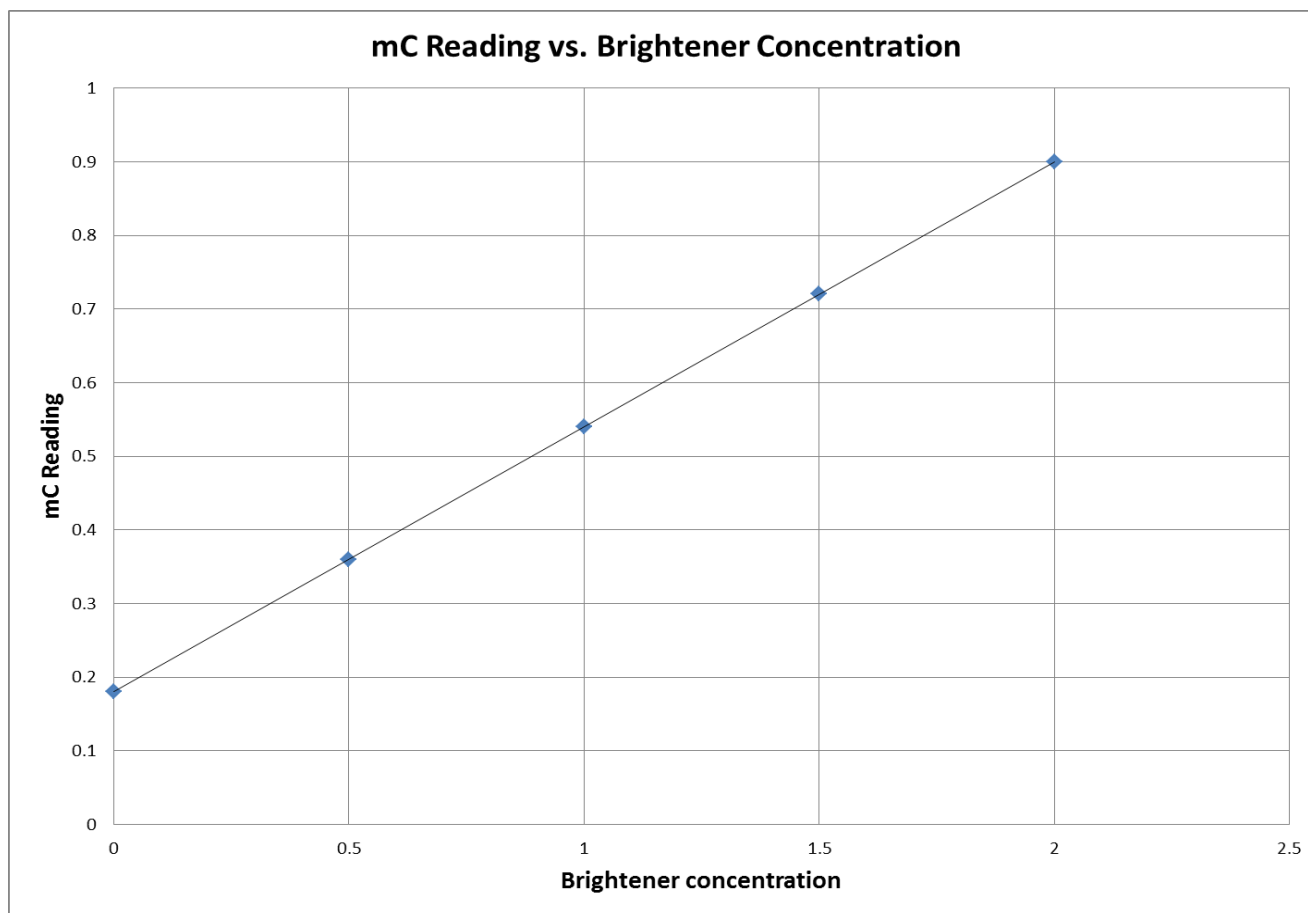
Suppressor Analysis: Std and Bath Sample



- ❖ A standard suppressor curve and a bath sample curve overlaid.



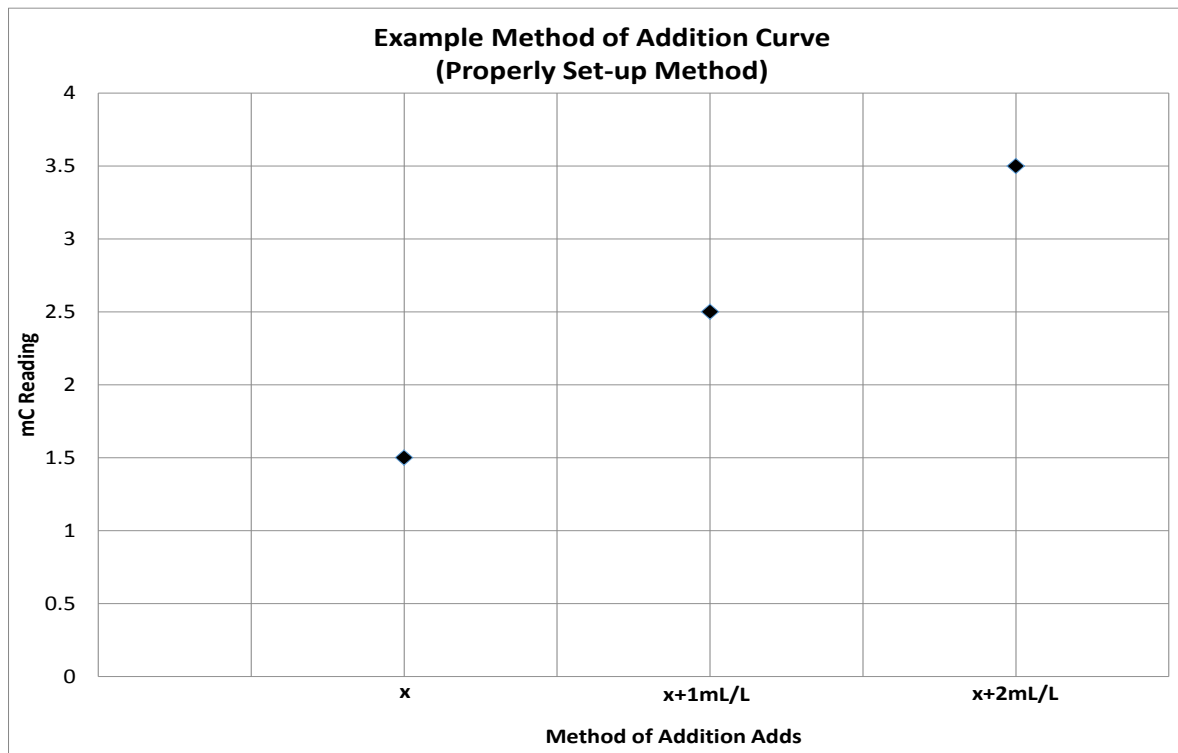
Brightener is Determined by Method of Addition



- ❖ Linear response to brightener additions (required)
- ❖ A Method of Addition is used to determine the brightener concentration of unknowns



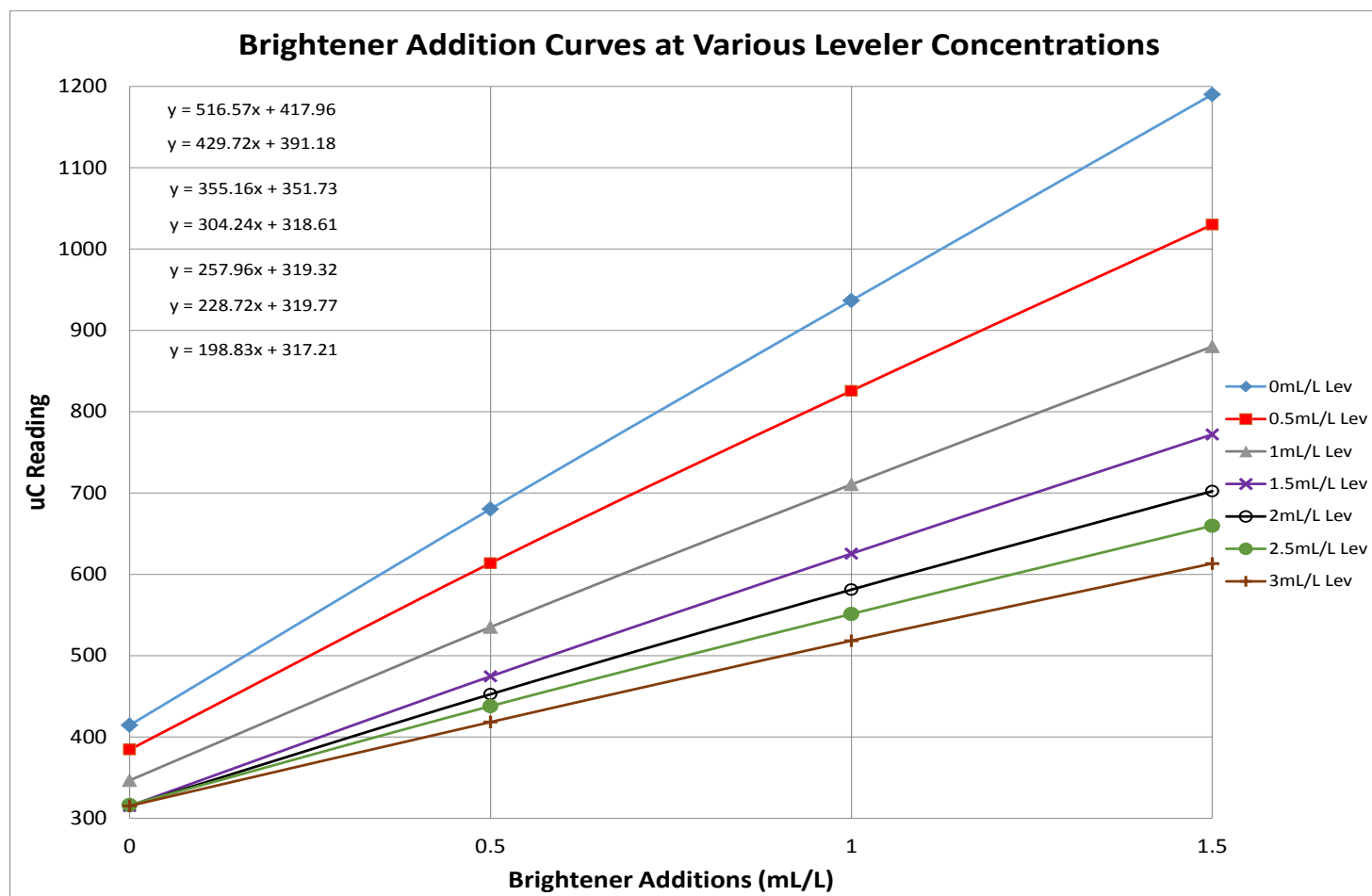
Example Method of Addition for Brightener



- ❖ Ideally the points are evenly spread with respect to the origin.
- ❖ Trial and error method may be required to optimize the procedure
- ❖ Determination of the correct Y intercept is critical
- ❖ Dilution of plating bath into fresh blank containing suppressor helps to better align brightener curve to correct intercept for accurate brightener determination



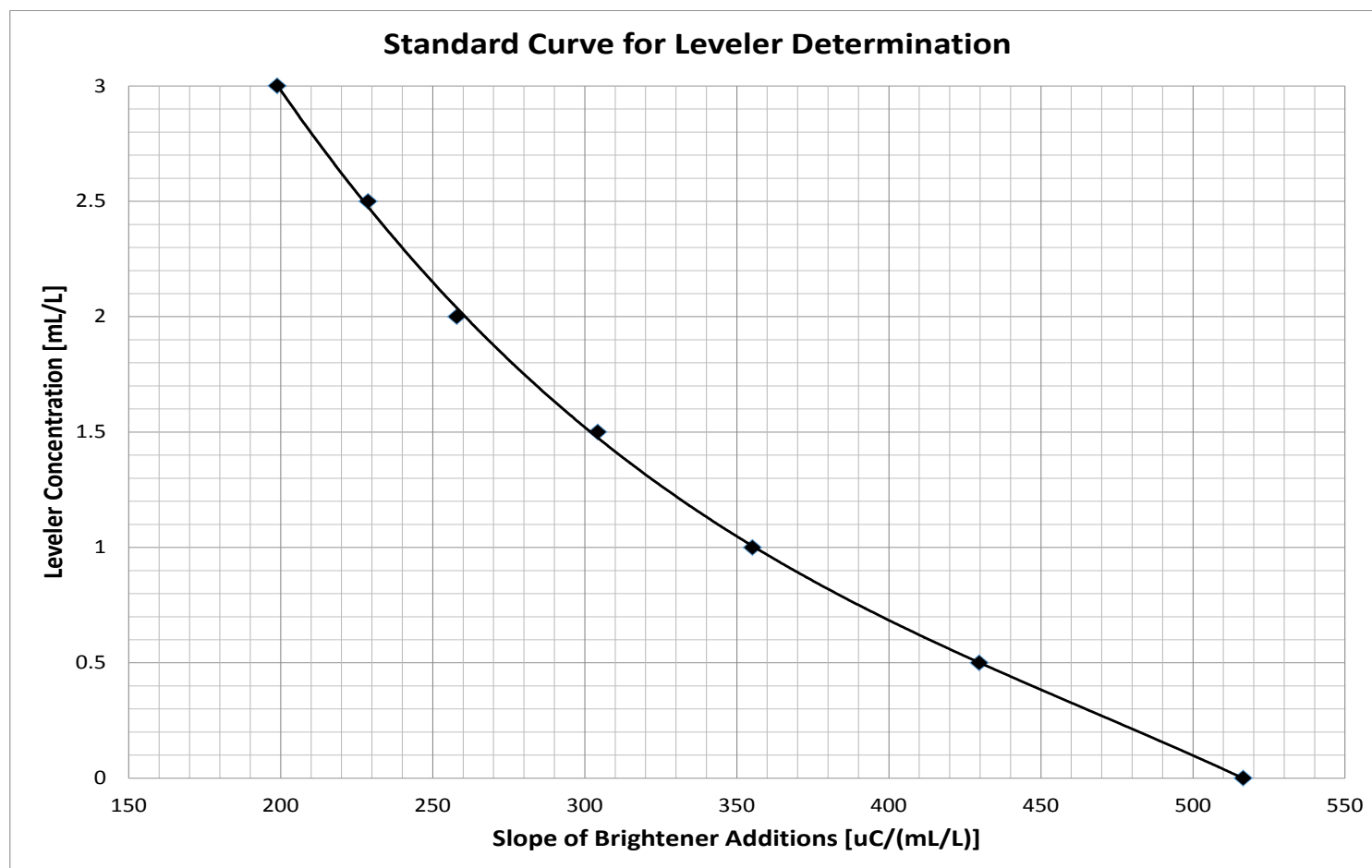
Effect of Leveler on Brightener Slope



❖ The concentration of the Leveler influences the slope of the brightener addition.



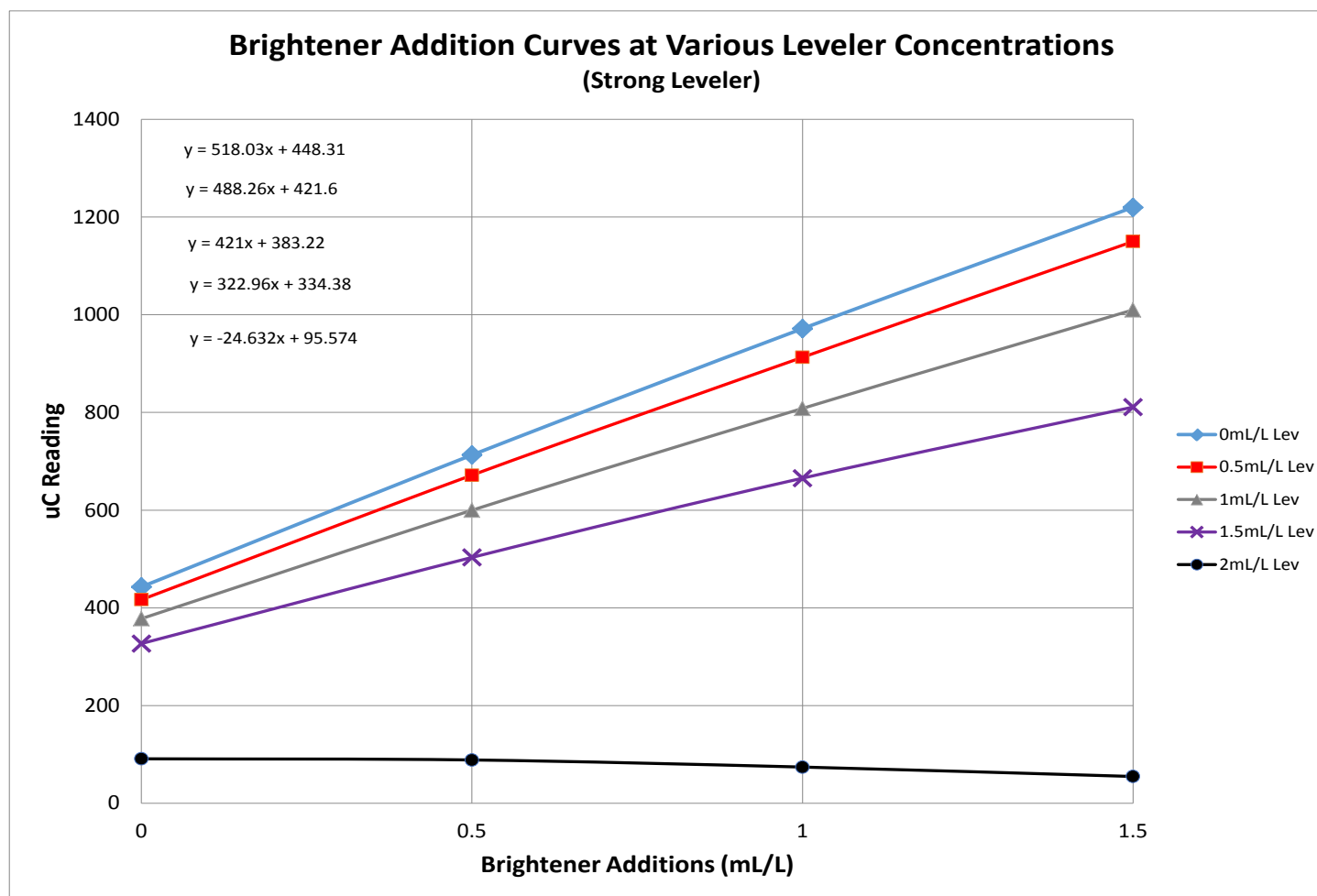
Standard Curve for leveler Determination



- ❖ The slope of brightener addition for each leveler std concentration is used to create a calibration curve for leveler determination.



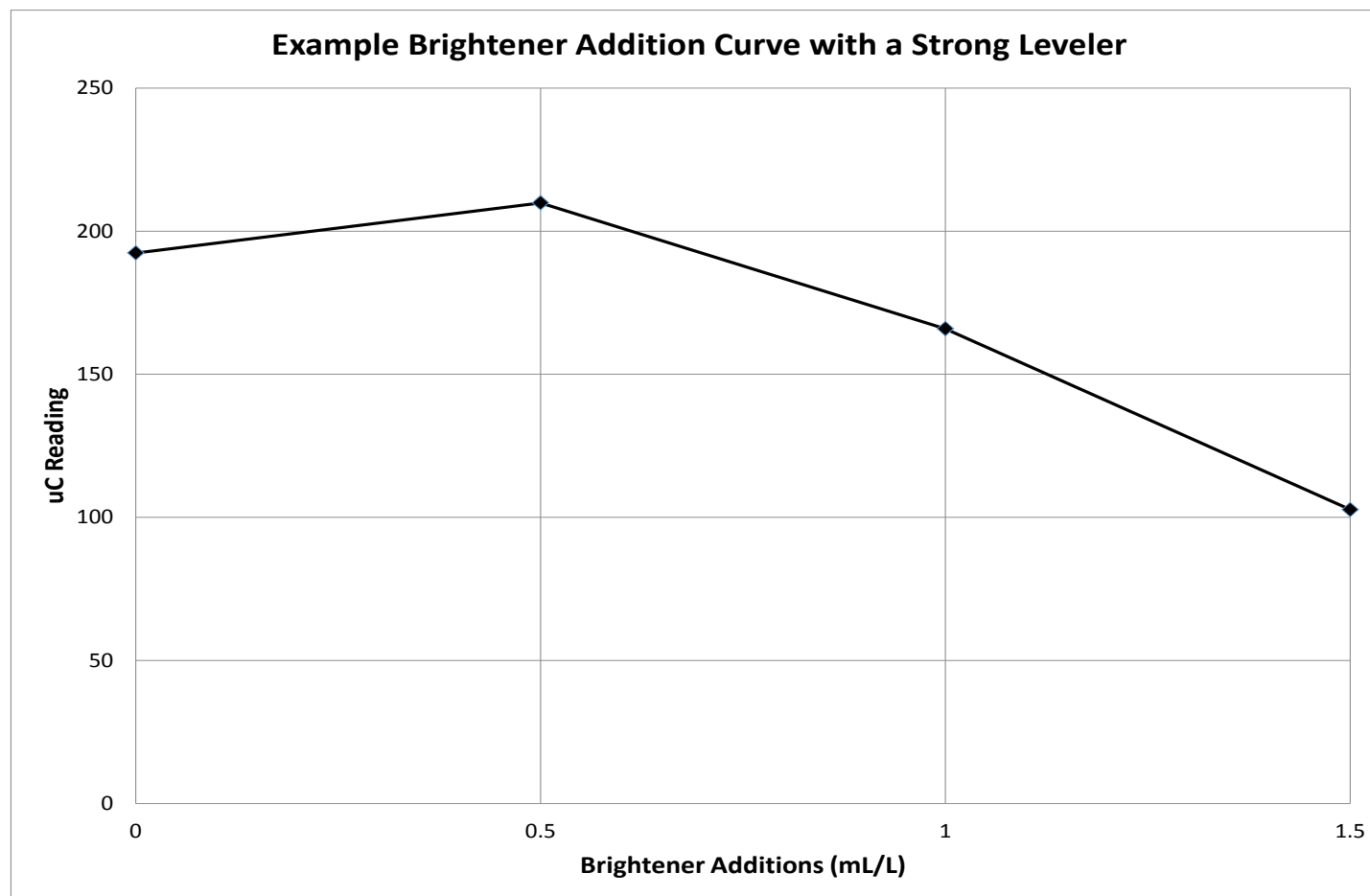
Brightener Addition Slopes for a Strong Leveler



❖ Different levelers will have different effects on brightener addition slopes.



Brightener Analysis Curve When High Concentrations of a Strong leveler are Present



- ❖ The brightener cannot be analyzed with this procedure due to the strong influence of the leveler component.



Problems with the Leveler Influencing the Brightener Analysis

- ❖ Some levelers can render brightener analysis impossible by CVS.
- ❖ Usually diluting the bath sample into the blank solution (with suppressor added) will allow for proper brightener analysis.
- ❖ The optimum dilution factor needs to be carefully considered.
- ❖ Diluting the sample improves the alignment with the Y intercept for method of addition.
- ❖ Diluting the sample too much may lower the bath mC reading to a value not significantly different than the Y Intercept.
- ❖ For high leveler to brightener ratios it is possible that no dilution will rescue the brightener analysis.



Effect of a Strong leveler on Subsequent Conditioning Scans

- ❖ A strong leveler may remain on the electrode surface even after rinsing the probes for the next analysis.
- ❖ The best way to remove the leveler is to run the condition, rinse again, and run conditioning again with fresh plating blank.

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Conclusions

- ❖ Proper CVS control of via fill plating baths is critical to success.
- ❖ A new method for determining the leveler concentration independent of the brightener concentration has been developed.
- ❖ All components can be accurately measured if the proper CVS techniques are developed.
- ❖ Some plating levelers can influence the accuracy of brightener determination in CVS analysis.
- ❖ Careful consideration and monitoring of the actual procedures, mC values obtained, addition and dilution amounts is required to optimize and properly maintain CVS analysis.