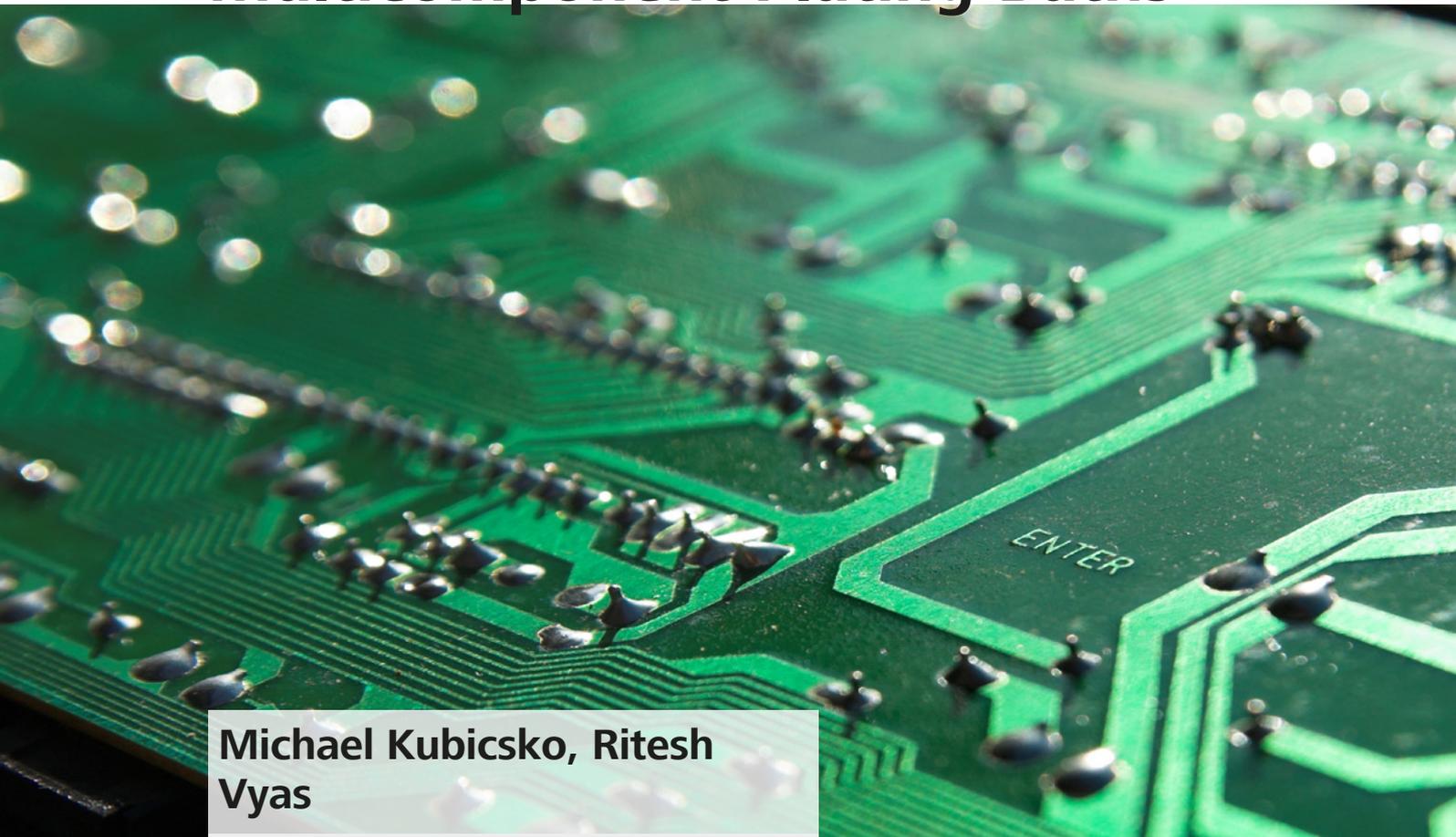


## Automated CVS Method Development and Optimization of Multicomponent Plating Baths



**Michael Kubicko, Ritesh Vyas**

Over the past three decades, the Cyclic Voltammetric Stripping (CVS) based analysis of organic additives in electroplating copper baths has been the standard practice in the circuit board and wafer plating industries. The process of developing methods to accurately analyze each individual component has become more tedious as the additive systems themselves have become more complex.

The variations in the compositions of such baths have created a need for more optimized method development routines. New advancements in the hardware and software protocols for CVS have simplified the overall process of method optimization to a great extent. In this study, the process of method optimization is discussed in conjunction with these protocols. Two different plating bath systems were analyzed to differentiate the challenges in method optimization.



## Cyclic Voltammetric Stripping Technique

Cyclic Voltammetric Stripping (CVS), and the related Cyclic Pulse Voltammetric Stripping (CPVS), have been the standards in the market place for analyzing the organic additives in copper plating baths. Both CVS and CPVS measure the charge (Q) required to strip the copper deposited on a rotating disc electrode (RDE). While CVS measures the current response over a voltage range at a defined sweep rate, the CPVS technique

measures the current response at corresponding voltage intervals and times.

The influence of the additives is easiest to observe during the earliest stages of copper deposition. It is this phenomenon that the analyst utilizes to isolate the effects of the individual organic components.

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## Electrolytic Copper Deposition

Today's modern copper electroplating processes are often described as 3 component systems consisting of a suppressor/carrier, an accelerator/brightener and a leveling component. Controlling all 3 components is a key to assure that the electrolytic copper deposition process performs as specified. Earlier formulations combined two or more of these components into a single or dual additive system, and the ability to control the plating process was limited by the inflexibility inherent in these formulations.

The individual additives work synergistically within a plating bath to deposit copper with the appropriate characteristics and quality. Carriers/suppressors form a current suppressing film on the cathodic surfaces to be plated, forming a uniform boundary layer. Accelerators/brighteners act as «grain refiners», controlling the grain structure and thus the physical properties of the deposit. Levelers also suppress plating primarily in «peak» areas, allowing the «valleys» to plate preferentially, ultimately producing a bright, reflective surface.

The task of creating analytical procedures that accurately measure each of the three organic additives in an acid copper electrolyte has become a complex and time consuming exercise. The need to investigate the effects of voltammetric sweep parameters such as first vertex potential and rotation speed on electrolyte behavior is necessary in order to find the optimal conditions for «teasing out» the individual additive's effect.

In this paper, it will be shown how advancements in hardware, software and liquid handling collectively contribute to efficient data collection in the course of developing procedures, and later be used to test the robustness of the procedure over variations in electrolyte composition. Two different multicomponent plating baths were tested. In developing the methods for each of these baths, the differences between the chemistries also became readily apparent.



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## Hardware Set-up

A Metrohm 894 Professional CVS System was utilized to conduct the testing and data collection. Peripheral equipment attached to the system included Dosinos for the accurate dispensing of standard and supporting electrolytes, and a pump station to assure consistent rinsing of the measuring cell between test runs. As an option for higher throughput one can also take advantage of a sophisticated sample changer.

The tools made available by the capabilities of the 894 Professional CVS and the **viva** software facilitated the method development process by enabling the automated, rapid collection of data for analysis.



**Figure 1.** 894 Professional CVS fully automated with 858 Professional Sample Processor, Dosinos and 843 Pump Station

## Software Set-up: viva

The 894 Professional CVS System is controlled by the **viva** software. The software includes an integrated method editor for customizing methods to facilitate testing. Some of these edits include the ability to vary such parameters as rotation speed and first vertex potential as well as to add synthetic bath samples to the measuring cell for analysis through the Dosinos, and varying those make-ups through the use of «sample data variables». Together with the optional pump station, several tests can be run consecutively in a «determination series», to provide the analyst an automated way to collect data for later review.

The basic methods are provided as templates. Depending on the accessories configured with the system, the analyst has the freedom to edit methods and parameters within methods to facilitate the experimental design.

The main track in any method contains the basic steps which the system executes to fulfil the given procedure. Each step is executed sequentially, often referring to other normal tracks within the method. Whether in the main track or one of the other normal tracks, parameters can remain «fixed» or made «variable» according to the needs of the user. With the appropriate accessories, tasks can then be automated in such a way that multiple experiments can be run to test the effects of various combinations of parameters.

For instance, pumps can be added to the system to facilitate the cleaning and rinsing of the measuring cell between analyses. Steps can be added to the main track to drain the measuring cell before the analysis begins, and rinse the cell at the end. With the pumps in place, it now becomes possible to run multiple tests as part of a series of experiments without an operator present.

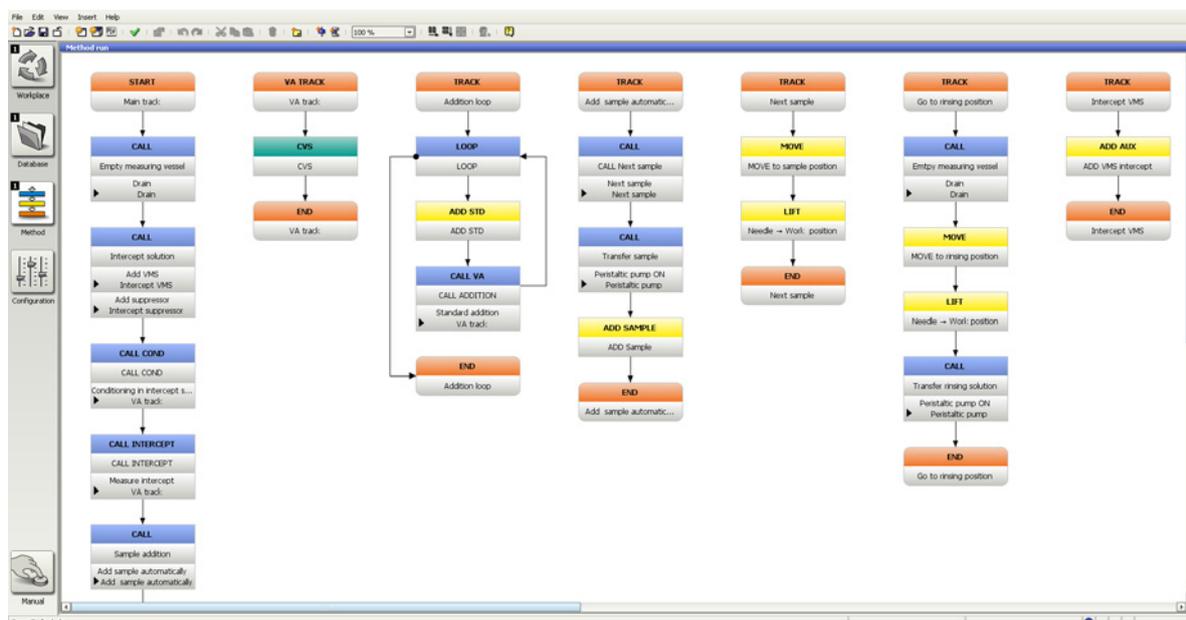


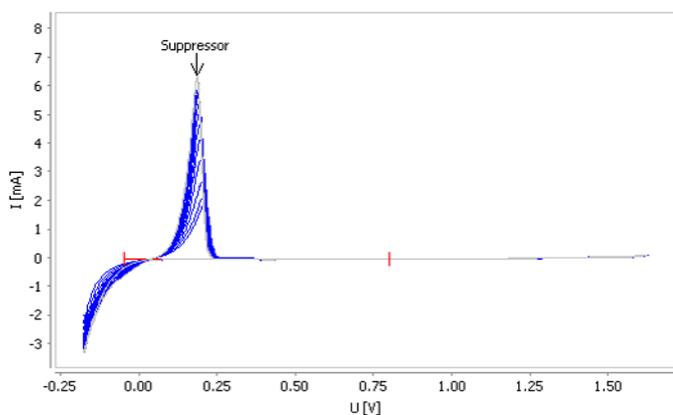
Figure 2. Method editor in **viva**

## Suppressor Analysis by Dilution Titration Technique

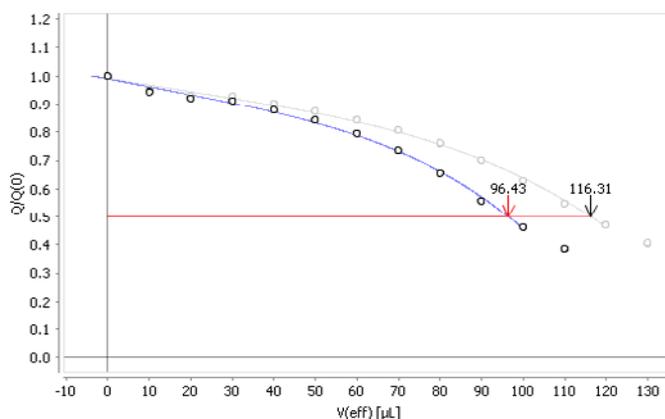
The Dilution Titration technique is typically used for measuring the suppressor component in an acid copper electrolyte. Adding a «suppressor» in small increments to a copper plating solution without organic additives reduces the stripping peak. With a calibration solution, a calibration curve can be established which is then compared to a sample of unknown concentration. Selecting an appropriate evaluation point, the volumes of standard and sample are compared, and a result is calculated. Optimizing the method depends on determining a proper first vertex potential, rotation speed and addition volume. The resulting Dilution Titration curve from the standard solution can then be used to define a proper evaluation ratio.

The standard Dilution Titration calibration method was modified in the software as follows.

- Addition of pump station for rinsing and draining of the sample vessel.
- The use of the sample data variable «Rotation Speed» to vary the rate of rotation for each test run.
- The use of the sample data variable «First Vertex Potential» to vary the negative limit on the sweep for each test run.
- The setting of the addition ratio to 0.3 to determine the best point to use as the evaluation ratio.



**Figure 3.** Typical CVS voltammogram of a suppressor determination using Dilution Titration (DT)



**Figure 4.** Typical CVS calibration and determination curves of a suppressor determination using Dilution Titration (DT)

## Results and Observations

Dilution Titration calibration curves for two different plating baths – can you explain what chemistry they are, varying both rotation speed and first vertex potential. Differences in the bath formulations yield different responses under similar conditions. The arrows show appropriate evaluation criteria

to be used when analyzing these baths. An ideal evaluation point is one in which a change in response is noted with the addition of standard, yet not so close to an inflection point where the evaluation point can be missed.

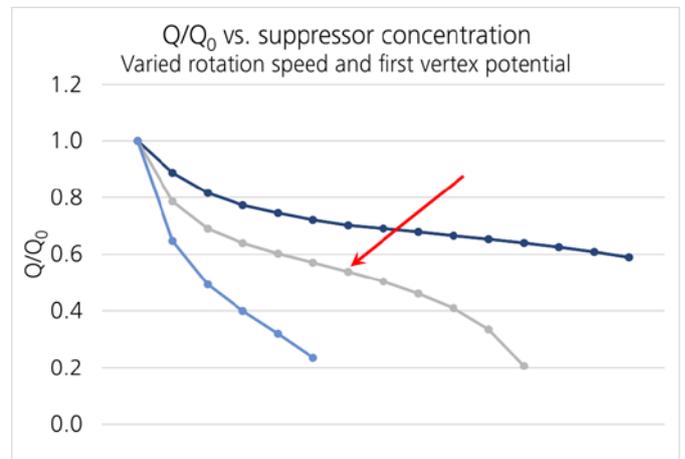
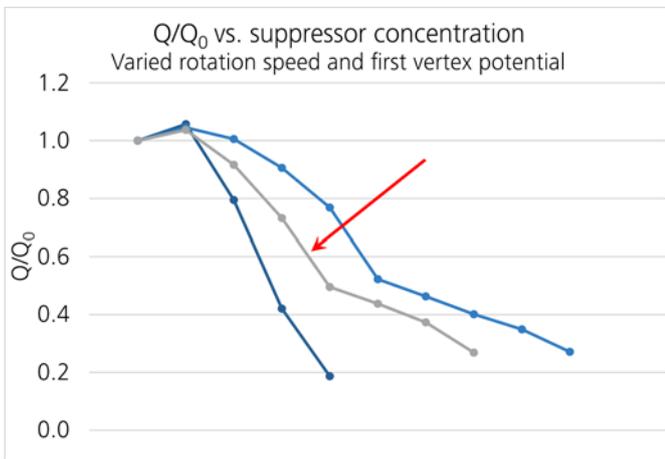
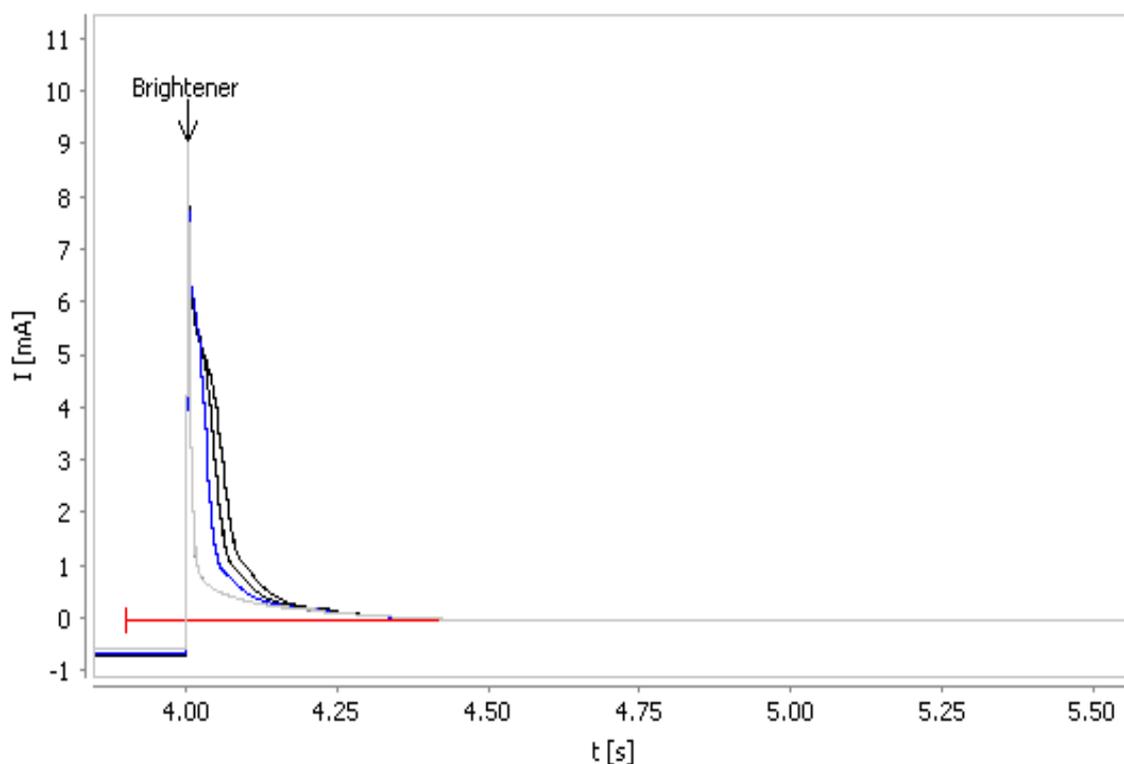


Figure 5. Dilution Titration curves for two different plating baths

## Brightener Analysis by Modified Linear Approximation Technique

The Modified Linear Approximation Technique (MLAT) is used for analyzing the accelerator/brightener component in an acid copper plating system. It is a technique which uses standard additions of the accelerator to back calculate the sample's concentration. An intercept solution is created and measured to establish the system response when no brightener is in the test solution.

The bath sample is then added and its response is measured as well. After two standard additions of the accelerator/brightener component, a result is calculated. As implied by the name, the technique requires that the stripping peak response be linear with respect to brightener concentration.



**Figure 6.** Typical CPVS chronoamperogram of a brightener determination using Modified Linear Approximation Technique (MLAT)

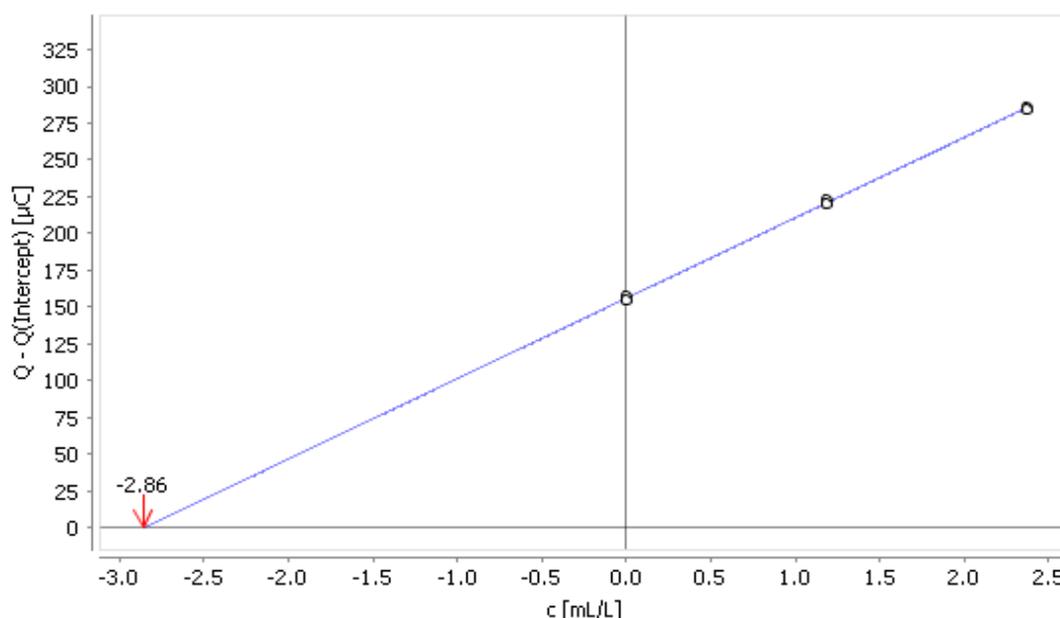
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Several steps are required to develop the method for a particular bath chemistry. They include:

- Creating and defining the intercept solution
- Determining the linear range for brightener response
- Optimizing sample volume and addition volume
- Deciding between CVS and CPVS
- Optimizing the first vertex potential, sweep rate and rotation speed (CVS)
- Optimizing the plating potential, time, and rotation speed (CPVS)

For each step in the process, sample data variables can be utilized to facilitate the data gathering process. Beginning with determining the suppressor concentration for the intercept solution, standard additions of suppressor can be added to the measuring cell. In the case of an additive system with both carrier and leveler, these adds can be made simultaneously or separately to assess the overall impact on the definition of the intercept solution.

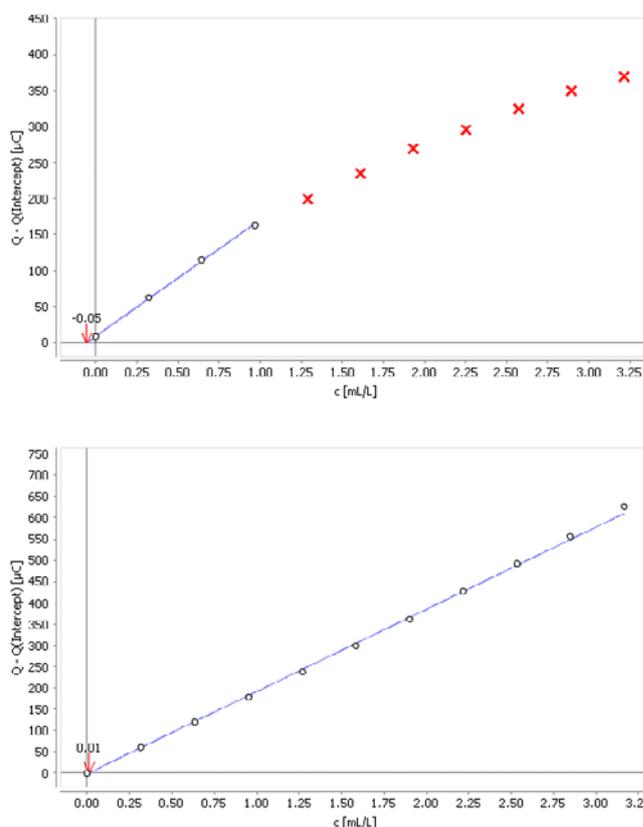
After defining the intercept solution, the next step is to determine the concentration range in which the response of the stripping peak,  $Q$ , is linear with respect to the concentration of brightener in the measuring cell. Here we want to see the impacts of CVS (first vertex potential and rotation speed) vs. CPVS (plating time and rotation speed). The use of sample data variables, with small additions of brightener facilitates the data gathering. Once the experiments are complete, **viva's** recalculation feature permits the user to systematically remove data to determine to what concentration level the  $Q$  values remain linear. With the linearity coefficient calculated automatically by the software, it is easy to find what parameters offer the best conditions for defining a robust method.



**Figure 7.** Typical standard addition curve of a brightener determination using Modified Linear Approximation Technique (MLAT)

With the conditions defined (intercept solution, first vertex potential, rotation speed, linearity range, for CVS or CPVS) creating the method becomes relatively straightforward. Following these guidelines will help faster method optimization.

- A minimum volume of 15 mL is needed to immerse the electrodes and measure the stripping peak. Use this as a starting volume for the method.
- Take the maximum concentration at which the Q response remains linear.
- Divide that concentration by 3. This defines the brightener concentration target in the measuring cell after dilution with the intercept solution.
- Divide the target concentration by the nominal bath concentration. This result provides the ratio of sample to the total volume of sample plus intercept solution in the measuring cell.
- Define the standard addition volume first by multiplying the target concentration in the measuring cell by 0.75, then multiplying that number by the total volume (bath plus intercept solution volumes) in the measuring cell.



**Figure 8.** Comparing the linear response of brightener to Q values of chemistry 1, we find that with this particular chemistry, the response is linear up to 3 mL/L in CPVS mode (bottom graph) vs. 1.0 mL/L in CVS mode (top graph). The implication is that a larger sample volume relative to the volume of intercept solution can be used and help minimize the impact of normal variations in sample preparation on the overall result.

## Results and Observations

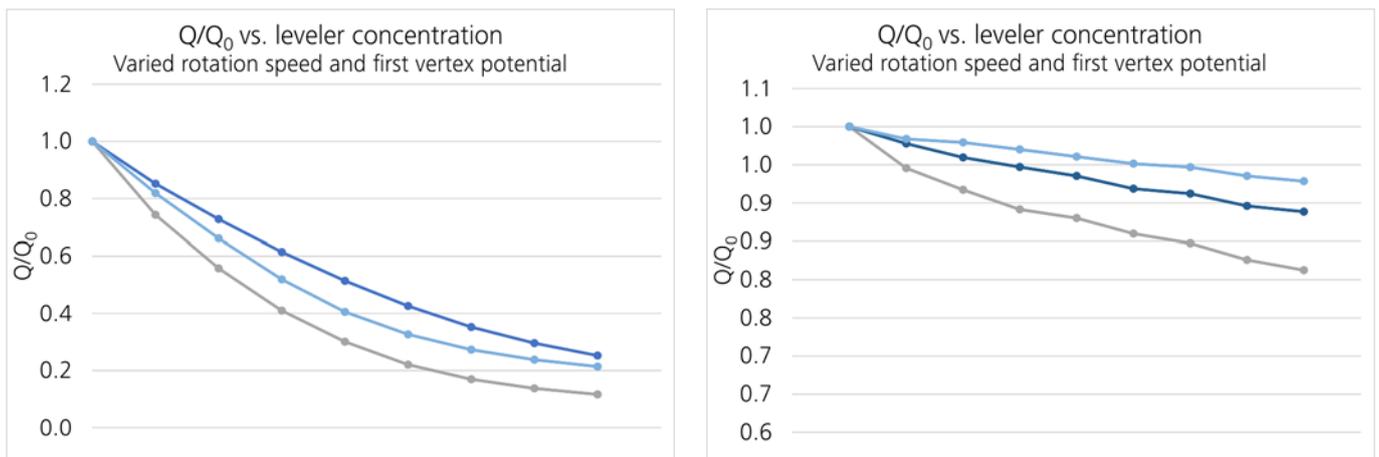
Testing the method with a variety of samples can easily be expedited and automated through the software. Rather than making up several solutions with varying concentrations of accelerator/brightener, a «synthetic bath addition» step can be substituted in the method for the sample addition step.

The Dosinos add the requisite VMS and additives to the measuring cell prior to the sample measuring step. In this way, multiple «samples» can be tested without the need for individually making up and measuring out the samples. More data, less waste.

## Leveler Analysis by Response Curve Technique

The Response Curve (RC) technique is a two-step process typically used for determining the leveler component in an acid copper system. The first step is the calibration curve derived from making standard additions of the leveler component to an electrolyte solution containing VMS, carrier/suppressor and accelerator/brightener. Normalizing the stripping response from the standard additions of leveler to the leveler free electrolyte, a calibration curve is developed.

During the actual analysis, the bath sample is then added to a fresh electrolyte solution and, accounting for dilution, the leveler concentration can be determined by comparing the result to the initial calibration. In addition to the sweep parameters used, one also needs to consider the composition of the electrolyte to assert minimal influence due to matrix effects.



**Figure 9.** The response calibration curve for chemistry 1 (left) shows a strong response to changes in leveler concentration as compared to chemistry 2.

With the Response Curve technique, we are mainly concerned with finding the voltammetric sweep parameters that provide a calibration curve with adequate slope. In particular, the developer needs to know how influential rotation speed and first vertex potential are on the measured stripping peaks. Setting these parameters as sample data variables and running a determination series provide the data needed.

Once the sweep conditions are set, the robustness of the method can be evaluated through the automatic make up of synthetic bath samples. Much as with the MLAT technique, sample data variables can once again be employed to test variations in the electrolyte on overall accuracy.

## Conclusions

The method development and optimization process for a multi-component analysis of typical acid copper bath is an increasingly complex endeavor. Given the multitude of parameters to consider and the influences caused by variations in additive concentrations themselves, the greatest challenge often at times is to measure the reproducibility of a built procedure subjected to various conditions.

In this work, apart from the newly developed procedures, it was also possible to develop a more direct protocol to apply these methods not only at nominal conditions, but also under a stress due to variances in any of the parameters under consideration. Equipped with this new tool, the bath suppliers and users both can experience increased confidence in their ability to control their processes, and thereby maintain their product quality.

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