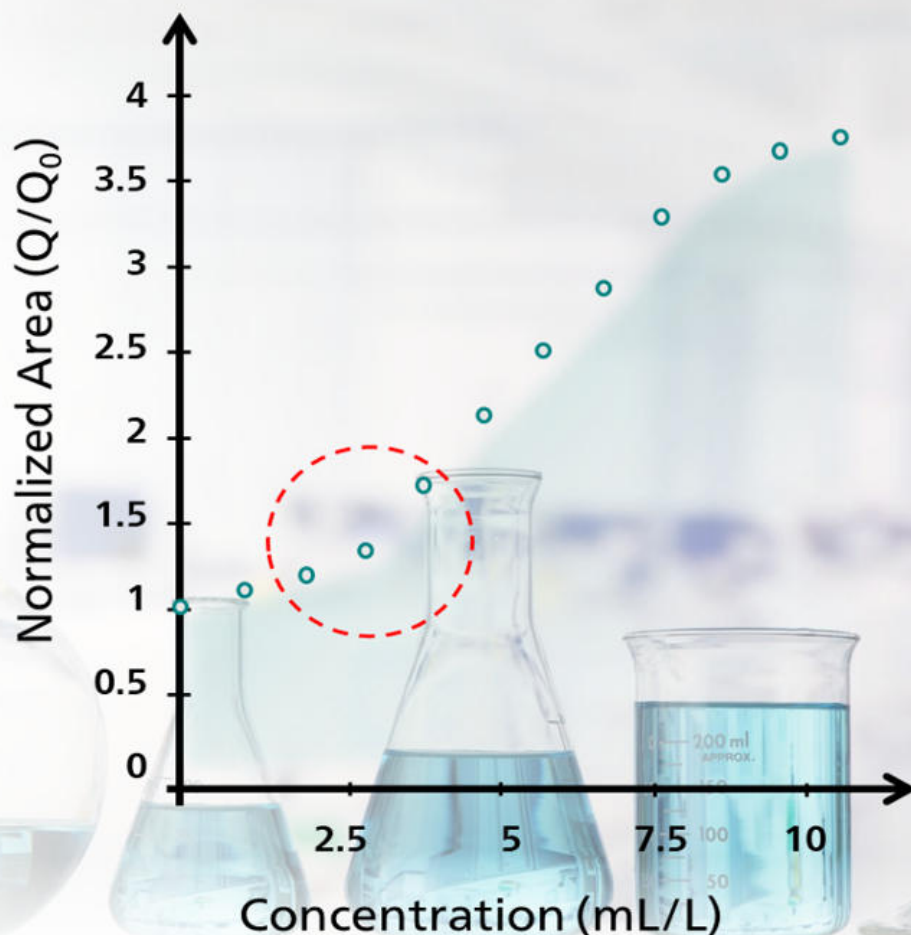




Application Note AN-V-242

brightRC – Advanced brightener analysis with a response curve

Next-level brightener determination in nonlinear systems

Reliable additive control is essential in acid copper plating processes. Suppressors, brighteners, and levelers directly influence functional properties of the deposit. Cyclic Voltammetric Stripping (CVS) is the industry standard technique to monitor the concentration of organic additives in copper plating solutions. For brightener (accelerator) type additives, the copper stripping signal increases with increasing additive concentration. Therefore, brightener determination is generally performed using standard addition techniques such as MLAT or LAT.

These require standard additions for each sample and rely on linear response behavior, limiting analytical flexibility and increasing analysis time. External calibration eliminates the need for repeated standard additions, enabling reliable analysis of brighteners that display nonlinear response behavior. The so-called response curve (RC) calibration approach allows the use of flexible regression models, improving electroplating process control efficiency. This functionality is available as a native feature in our CVS software, **viva** 4.0 and up.

brightRC is a response curve calibration approach for the determination of brightener-type additives by CVS or CPVS (Cyclic Pulse Voltammetric Stripping), hence the name «brightRC». This technique is suitable to measure brightener content in copper baths for plating. The method is based on signal normalization using the electrolyte value, which is the response for the virgin makeup solution (VMS) saturated with suppressor, and brightener defined as Q_0 in the **viva** software. All recorded signals are divided by Q_0 and the normalized values are plotted against concentration to generate an external calibration curve. This calibration can then be used for routine sample determination without repeated standard additions.

The sample is simply measured using the same method as the calibration, signals are normalized and evaluated using the mathematically fitted calibration curve. By decoupling calibration from sample

measurement, brightRC removes the need for repeated standard additions with each sample measurement, enabling faster and more efficient routine analysis.

The brightRC calibration approach supports flexible regression models including quadratic and nonlinear regression. This allows reliable quantification of additive systems that do not exhibit a wide linear working range or exhibit nonlinear response characteristics, thereby expanding the range of applicable brightener chemistries.

One important detail that further differentiates brightRC from the MLAT approach relates to normalization of the signal for calibration and sample analysis. This normalization approach improves measurement robustness as variations in absolute signal intensity naturally occurring over the working day are mathematically compensated.

HOW DOES BRIGHTRC WORK IN PRACTICE?

The brightRC workflow separates calibration and sample analysis. It can be implemented in different setups (from manual to fully automated) depending on the additive system and concentration range.

After recording the electrolyte value, calibration standards are measured to establish the calibration curve, otherwise known as the response curve. Once the calibration is stored, samples are determined with the same CVS or CPVS method, without further standard additions. The sample concentration is automatically calculated from the normalized signal using the calibration curve.

For sample measurement, **viva** 4.0 provides two practical approaches:

1. «brightRC with solution exchange»

2. «brightRC with sample dilution»

Both variants follow the same calibration principle and differ only in the sample handling strategy.

USING BRIGHTRC FOR NONLINEAR BRIGHTENER BEHAVIOR

Figure 1 illustrates the impact of nonlinear signal behavior on the quantification of brightener additives when using different calibration approaches. The model system (Figure 1A) shows a clearly curved calibration response, meaning that the signal increase is not proportional to concentration over the investigated range.

When applying a standard addition technique such as MLAT (Figure 1B), the sample signal and subsequent additions are evaluated using linear extrapolation.

However, because the signal increase between additions is not linear, the extrapolated intersection with the concentration axis deviates from the true value. This results in a systematic error in the calculated concentration. In contrast, brightRC evaluates the sample signal using the stored calibration curve (Figure 1C). The measured signal is directly projected onto the response curve, allowing accurate concentration determination without the need for a linear correlation.

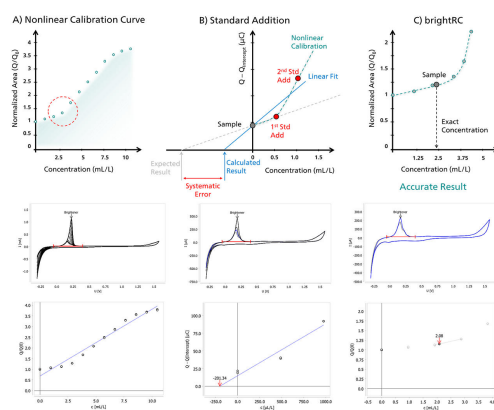


Figure 1. Conceptual comparison of standard addition and brightRC for a nonlinear brightener system. The presented data are based on a model brightener system.

RESULTS

This comparison demonstrates that for additive systems exhibiting nonlinear response behavior, the brightRC method provides more reliable results and

avoids the systematic deviations that can occur when standard addition techniques are applied to nonlinear systems.

WHEN TO USE BRIGHTRC?

brightRC is ideal for routine brightener control in stable plating baths where high sample throughput is required. It is particularly suitable when matrix conditions are consistent and electrode fouling is limited. The approach is especially advantageous for additive systems exhibiting nonlinear signal behavior.

If strong matrix variations, significant breakdown products, or severe electrode fouling are expected and a linear correlation between signal and analyte concentration is guaranteed, standard addition techniques such as MLAT are preferred because they may provide additional robustness.

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CONFIGURATION



894 Professional CVS fully automated for small sample series

Automated analysis system for the determination of organic additives in electroplating baths using CVS ("Cyclic Voltammetric Stripping"), CPVS ("Cyclic Pulse Voltammetric Stripping") and CP ("Chronopotentiometry"). Comprising 894 Professional CVS, 919 IC Autosampler plus, four 800 Dosinos, 843 Pump Station, measuring head for rotating disk electrodes and extensive accessories. For small sample series of up to 14 samples.

The viva software is required for control, data recording and evaluation. PC, electrode set and viva license are to be ordered separately.