# Temperature dependence of CVS determinations

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## Summary

An accurate, reproducible and reliable method for determining the organic additive content in acidic copper plating baths will increase the process stability during the production of printed circuit boards.

The CVS (cyclic voltammetric stripping) technique allows to simply measure and control the concentration of the used organic additives in acidic copper plating baths. The technique applies an indirect measurement that uses the influence of the organic additives on the copper plating process to determine the additive concentration. The quantity of organic additives as well as the temperature of the measuring solution affect the reaction kinetics. The reduction rate of the Cu ions increases with increasing temperature. Hence, the quantity of copper deposited increases and so does the resulting signal. The influence of the temperature of the measuring solution on the relationship between additive concentration and signal is shown in the first part. In the second part the influence of the temperature difference between sample and intercept solution was examined.

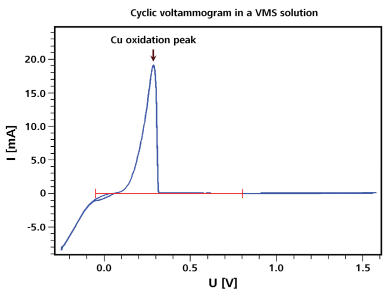
## Introduction

The ongoing miniaturization and increasing functionality of electronic devices such as mobile phones or minicomputers require maximum utilization of the space on a printed circuit board. To obtain a higher number of electrical connections, modern layouts of printed circuit boards increase the number of connecting vias with a simultaneous decrease of the interconnection distances. To realize such an increase in complexity, the production of printed circuit boards has to meet exacting requirements.

One of the most important process steps in the manufacturing of printed circuit boards is galvanic copper plating of the drill holes and the board surface. By the use of organic additives (suppressor and brightener) the physical properties of the plated copper can be adjusted and controlled.

The cyclic voltammetric stripping (CVS) technique is employed to determine the concentration of the organic additives. The CVS technique is based on an indirect measurement that uses the influence of the organic additives on the copper plating process to determine the additive concentration. Thus, for example, the quantity of the plated copper is reduced by the addition of suppressor. The addition of brightener to a copper solution saturated with suppressor increases the quantity of the plated copper.

The concentration of the organic additives is quantified by different calibration techniques.



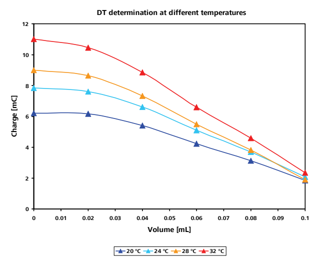

## Temperature dependence of the suppressor determination using DT/CVS

For the investigation of the temperature influence on the suppressor determination by means of dilution titration (DT) in the CVS mode, calibration and determination curves of a standard solution were recorded. In order to make a realistic statement, a temperature range of 20 to 32 °C was selected. Four calibration curves at a measuring solution temperature of 20, 24, 28 and 32 °C were recorded. With increasing temperature the dilution titration curve gets steeper. The evaluation criterion of 50% of the initial signal is obtained with a smaller addition of standard solution. From this it can be concluded that with increasing measuring solution temperature the inhibiting effect of the suppressor additive increases. Consequently, four determinations were recorded using the same four measuring solution temperatures as already applied to obtain the calibration curves. A crosswise recalculation of the results with the different calibrations resulted in:

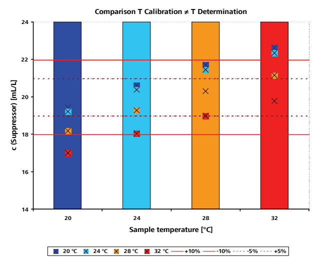
Recovery rate between 90 and 110%

if

T (determination) ≤ T (calibration) ± 8 °C




The resulting signal and curve shape of a dilution titration is influenced by the temperature of the measuring solution.




If the temperature difference between calibration and determination ≤ 8 °C, the results stay within ± 10% of the expected result.

### Crosswise recalculation of the results

| | | Calibration | | | |
|---|---|---|---|---|---|
| | | 20 °C | 24 °C | 28 °C | 32 °C |
| Recovery rate | 20 °C | 97.2% | 96.1% | 90.9% | 85.0% |
| | 24 °C | 103.1% | 101.9% | 96.4% | 90.1% |
| | 28 °C | 108.6% | 107.3% | 101.5% | 94.9% |
| | 32 °C | 113.1% | 111.7% | 105.8% | 98.9% |

$T_{(sample)} = T_{(intercept\ solution)}$ | Recovery rate = 100 ± 10% | Recovery rate < 90% or > 110%

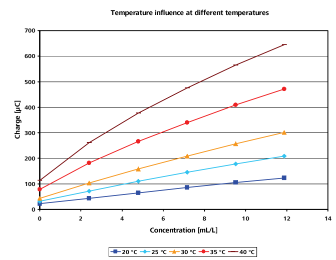
## Temperature dependence of the brightener determination using MLAT/CPVS

The quantification of the brightener concentration is based on the standard addition technique, which assumes a linear correlation between concentration and signal. To obtain information about the temperature dependence of the correlation between signal and concentration (linearity) of the brightener determination, standard addition curves for a concentration range of 0…12 mL/L were recorded at temperatures of 20, 25, 30, 35 and 40 °C.

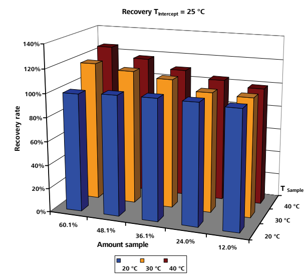
No linear correlation between signal and concentration could be observed for temperatures of the measuring solution above 30 °C.

The temperature of the measuring solution is affected by the temperatures of the used auxiliary solution (intercept solution) and the added sample. To explore the influence of the sample temperature on the result, different mixing ratios of sample (12…60%) and intercept solution were tested at sample temperatures of 20, 30 and 40 °C. The temperature of the auxiliary solution was 25 °C.

It could be shown that the recovery rate of a standard solution exceeds 110% if the temperature difference between intercept solution and sample exceeds 10 °C and the sample fraction is higher than 48% of the entire measuring solution.




Increasing the temperature of the measuring solutions gives higher signals while the correlation coefficient decreases.




If the temperature difference between intercept solution and the sample exceeds 10 °C and the sample fraction is higher than 48%, the recovery rate will exceed 110%.

| Intercept solution | | Sample | | Recovery rate | | |
|---|---|---|---|---|---|---|
| mL | % | mL | % | 20 °C | 30 °C | 40 °C |
| 16.6 | 39.9% | 25 | 60.1% | 99.3% | 117.5% | 125.7% |
| 21.6 | 51.9% | 20 | 48.1% | 101.0% | 113.4% | 117.4% |
| 26.6 | 63.9% | 15 | 36.1% | 101.5% | 109.1% | 109.9% |
| 31.6 | 76.0% | 10 | 24.0% | 101.2% | 100.9% | 104.0% |
| 36.6 | 88.0% | 5 | 12.0% | 99.4% | 99.7% | 99.4% |



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