Temperature Compensation by Embedded Temperature Variation Method for an AC Voltammeric Analyzer of Electroplating Baths

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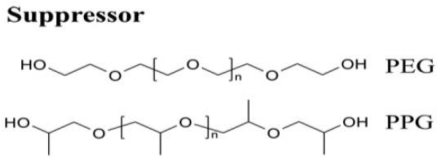
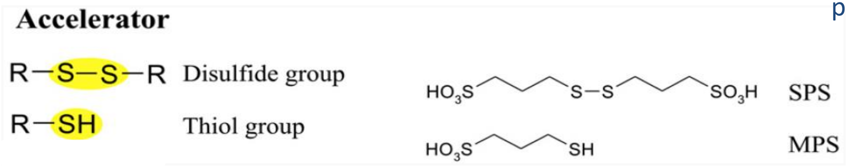
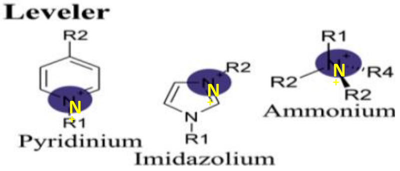
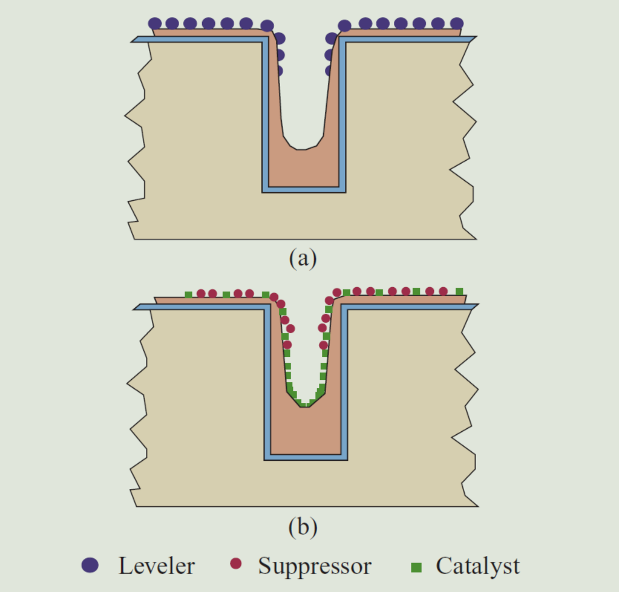
Typical Copper Plating Bath Composition

Copper	**Copper Sulfate**	0.25-1 mol/L
Acid	**Sulfuric Acid**	0.1-2 mol/l
Chloride	**Chloride Ion**	20-100 ppm
Suppressor		100s ppm
Accelerator		ppm(s)
Leveler		Wide (from sub-ppm to g/L)

Jaworski et al., 17th ESEAC, Rodos, Greece, June 3-7, 2018

Superfilling Mechanisms of Submicron Features

adsorption-based, temperature dependent



Strong adsorbing **Leveler** inhibits plating (by deactivating accelerator) in the field and at the mouth of the feature.
Diffusion-Consumption Model

Suppressor: adsorption instantaneous but weak, diffuses slowly, but moderately concentrated: adequate initial supply.

Accelerator: adsorption of moderate pace but strong, diffuses fast, but low concentration: insufficient initial supply, gradual displacement of suppressor, bottom-up plating
Curvature Enhanced Accelerator Coverage Model

P.M. Vereecken et al., *IBM J. Res. & Dev.* Vol. 49 No 1, January 2005, pp.3-18

"Simple System":
Cu^{2+}, H_2S0_4, Cl^-, suppressor, accelerator

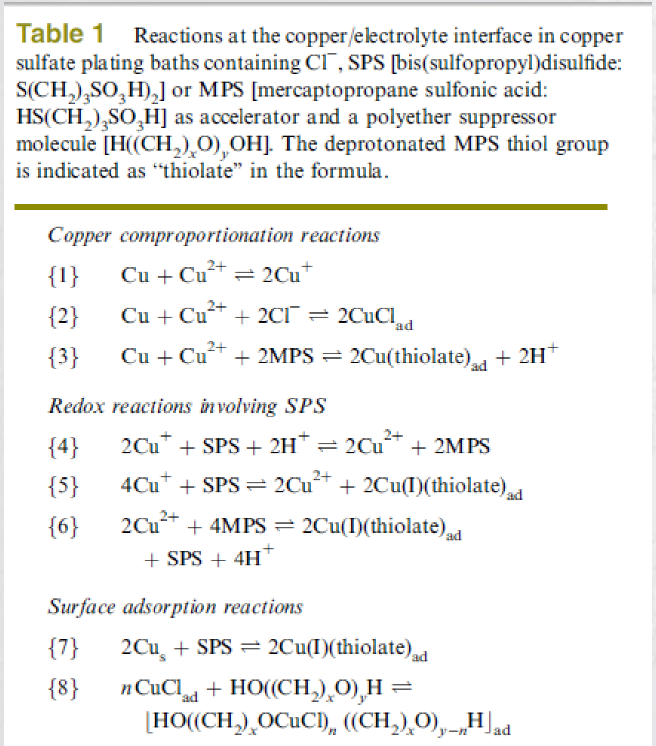


Table 1 Reactions at the copper/electrolyte interface in copper sulfate plating baths containing Cl^-, SPS [bis(sulfopropyl)disulfide: $S(CH_2)_3SO_3H)_2$] or MPS [mercaptopropane sulfonic acid: $HS(CH_2)_3SO_3H$] as accelerator and a polyether suppressor molecule [$H((CH_2)_xO)_yOH$]. The deprotonated MPS thiol group is indicated as "thiolate" in the formula.

Copper comproportionation reactions

{1} $\mathrm{Cu} + \mathrm{Cu}^{2+} \rightleftharpoons 2\mathrm{Cu}^+$

{2} $\mathrm{Cu} + \mathrm{Cu}^{2+} + 2\mathrm{Cl}^- \rightleftharpoons 2\mathrm{CuCl}_{ad}$

{3} $\mathrm{Cu} + \mathrm{Cu}^{2+} + 2\mathrm{MPS} \rightleftharpoons 2\mathrm{Cu(thiolate)}_{ad} + 2\mathrm{H}^+$

Redox reactions involving SPS

{4} $2\mathrm{Cu}^+ + \mathrm{SPS} + 2\mathrm{H}^+ \rightleftharpoons 2\mathrm{Cu}^{2+} + 2\mathrm{MPS}$

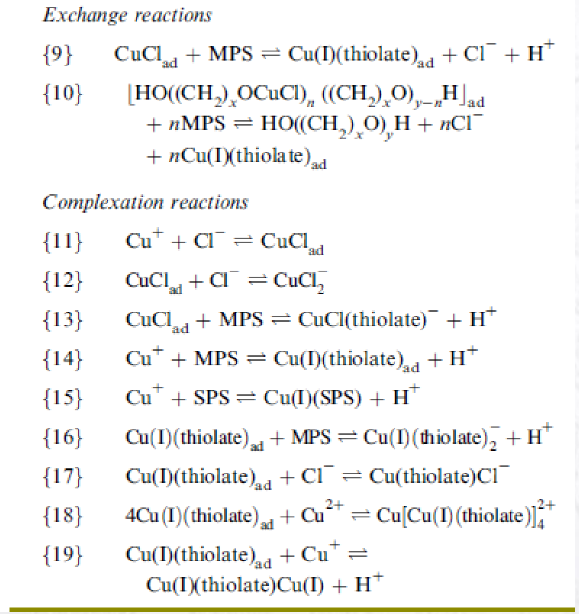
{5} $4\mathrm{Cu}^+ + \mathrm{SPS} \rightleftharpoons 2\mathrm{Cu}^{2+} + 2\mathrm{Cu(I)(thiolate)}_{ad}$

{6} $2\mathrm{Cu}^{2+} + 4\mathrm{MPS} \rightleftharpoons 2\mathrm{Cu(I)(thiolate)}_{ad} + \mathrm{SPS} + 4\mathrm{H}^+$

Surface adsorption reactions

{7} $2\mathrm{Cu}_s + \mathrm{SPS} \rightleftharpoons 2\mathrm{Cu(I)(thiolate)}_{ad}$

{8} $n\mathrm{CuCl}_{ad} + \mathrm{HO((CH_2)_xO)_yH} \rightleftharpoons [\mathrm{HO((CH_2)_xOCuCl)}_n\,\mathrm{((CH_2)_xO)}_{y-n}\mathrm{H}]_{ad}$



Exchange reactions

{9} $\mathrm{CuCl}_{ad} + \mathrm{MPS} \rightleftharpoons \mathrm{Cu(I)(thiolate)}_{ad} + \mathrm{Cl}^- + \mathrm{H}^+$

{10} $[\mathrm{HO((CH_2)_xOCuCl)}_n\,\mathrm{((CH_2)_xO)}_{y-n}\mathrm{H}]_{ad} + n\mathrm{MPS} \rightleftharpoons \mathrm{HO((CH_2)_xO)_yH} + n\mathrm{Cl}^- + n\mathrm{Cu(I)(thiolate)}_{ad}$

Complexation reactions

{11} $\mathrm{Cu}^+ + \mathrm{Cl}^- \rightleftharpoons \mathrm{CuCl}_{ad}$

{12} $\mathrm{CuCl}_{ad} + \mathrm{Cl}^- \rightleftharpoons \mathrm{CuCl}_2^-$

{13} $\mathrm{CuCl}_{ad} + \mathrm{MPS} \rightleftharpoons \mathrm{CuCl(thiolate)}^- + \mathrm{H}^+$

{14} $\mathrm{Cu}^+ + \mathrm{MPS} \rightleftharpoons \mathrm{Cu(I)(thiolate)}_{ad} + \mathrm{H}^+$

{15} $\mathrm{Cu}^+ + \mathrm{SPS} \rightleftharpoons \mathrm{Cu(I)(SPS)} + \mathrm{H}^+$

{16} $\mathrm{Cu(I)(thiolate)}_{ad} + \mathrm{MPS} \rightleftharpoons \mathrm{Cu(I)(thiolate)}_2^- + \mathrm{H}^+$

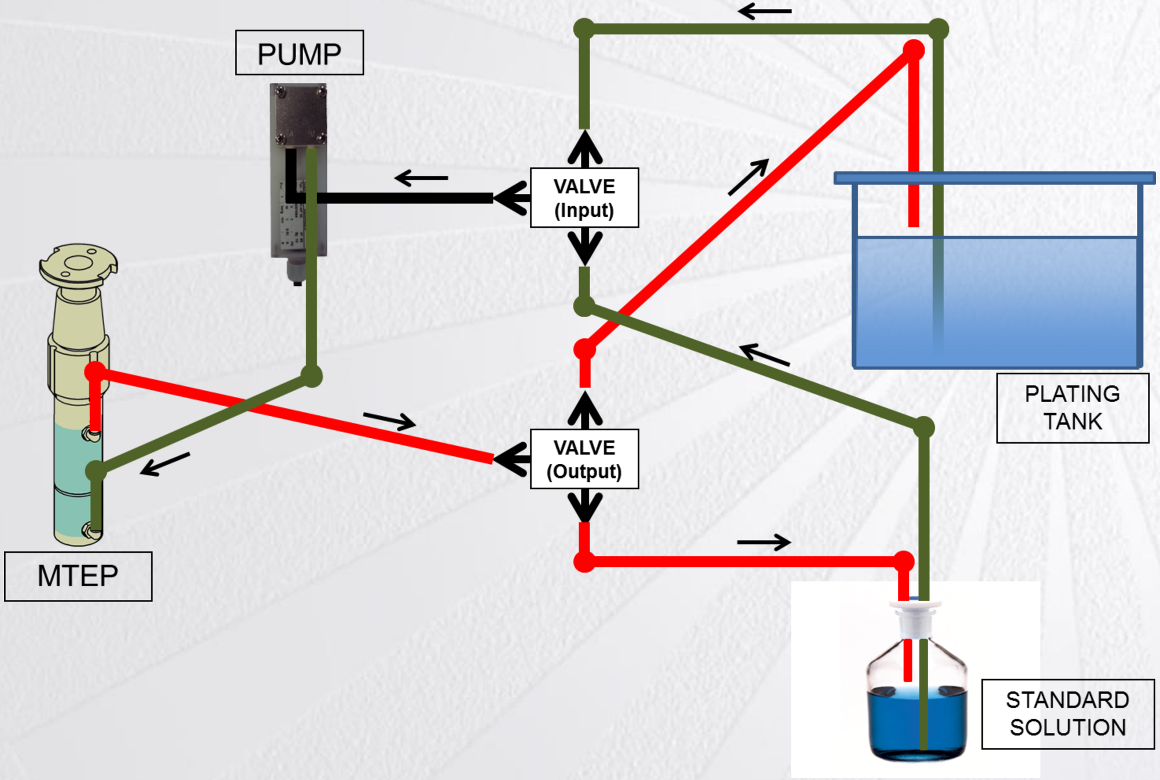
{17} $\mathrm{Cu(I)(thiolate)}_{ad} + \mathrm{Cl}^- \rightleftharpoons \mathrm{Cu(thiolate)Cl}^-$

{18} $4\mathrm{Cu(I)(thiolate)}_{ad} + \mathrm{Cu}^{2+} \rightleftharpoons \mathrm{Cu[Cu(I)(thiolate)]}_4^{2+}$

{19} $\mathrm{Cu(I)(thiolate)}_{ad} + \mathrm{Cu}^+ \rightleftharpoons \mathrm{Cu(I)(thiolate)Cu(I)} + \mathrm{H}^+$

P.M. Vereecken at al., IBM J. Res. & Dev. Vol.49 No 1 January 2005, p.3-18

Multitask Electrochemical Probe



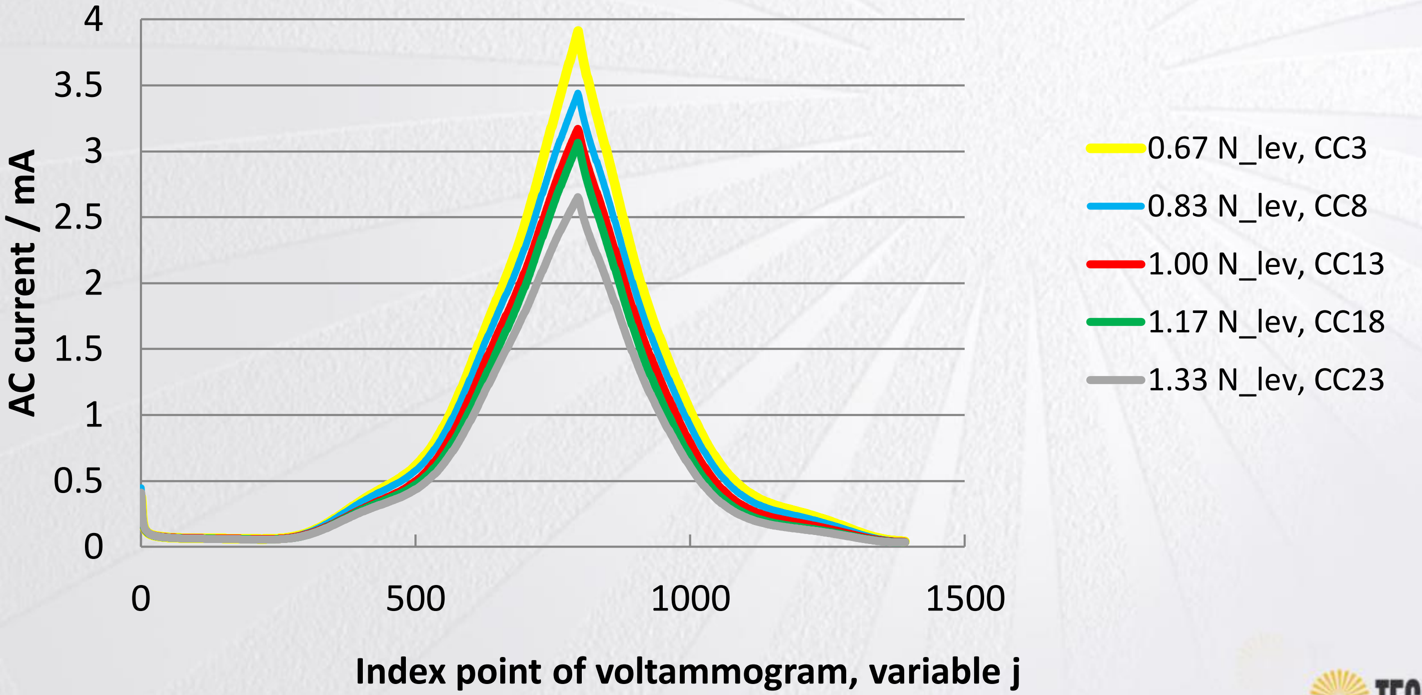
Jaworski et al., 17th ESEAC, Rodos, Greece, June 3-7, 2018

Two Training Sets: at constant temperature and with embedded temperature variation

Leveler, N_{Lev}	Suppressor, N_{Supp}	Accelerator, N_{Acc}	Temperature °C
0.67	0.50	0.67	19.0
0.67	1.50	0.83	20.0
0.67	1.25	1.00	21.0
0.67	1.00	1.17	22.0
0.67	0.75	1.33	23.0
0.83	1.00	1.33	19.0
0.83	0.75	0.67	20.0
0.83	0.50	0.83	21.0
0.83	1.50	1.00	22.0
0.83	1.25	1.17	23.0
1.00	1.50	1.17	19.0
1.00	1.25	1.33	20.0
1.00	1.00	0.67	21.0
1.00	0.75	0.83	22.0
1.00	0.50	1.00	23.0
1.17	0.75	1.00	19.0
1.17	0.50	1.17	20.0
1.17	1.50	1.33	21.0
1.17	1.25	0.67	22.0
1.17	1.00	0.83	23.0
1.33	1.25	0.83	19.0
1.33	1.00	1.00	20.0
1.33	0.75	1.17	21.0
1.33	0.50	1.33	22.0
1.33	1.50	0.67	23.0

Fundamental Frequency AC Cyclic Voltammogram: Dependence on Leveler Concentration

f=50 Hz, *φ*=0°, A=50 mV, v=50 mV/s, E_{ini}=0.8, E_{vertex}=0 V vs. $E_{Cu^{2+}/Cu}$



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Variable Selection Based on Leveler Impact Regression analysis of voltammetric data

$\boldsymbol{X}^{(I\times J)}$	voltammetric data matrix
$\boldsymbol{c}^{(I\times 1)}$	leveler concentration vector
$\boldsymbol{t}^{(I\times 1)}$	temperature

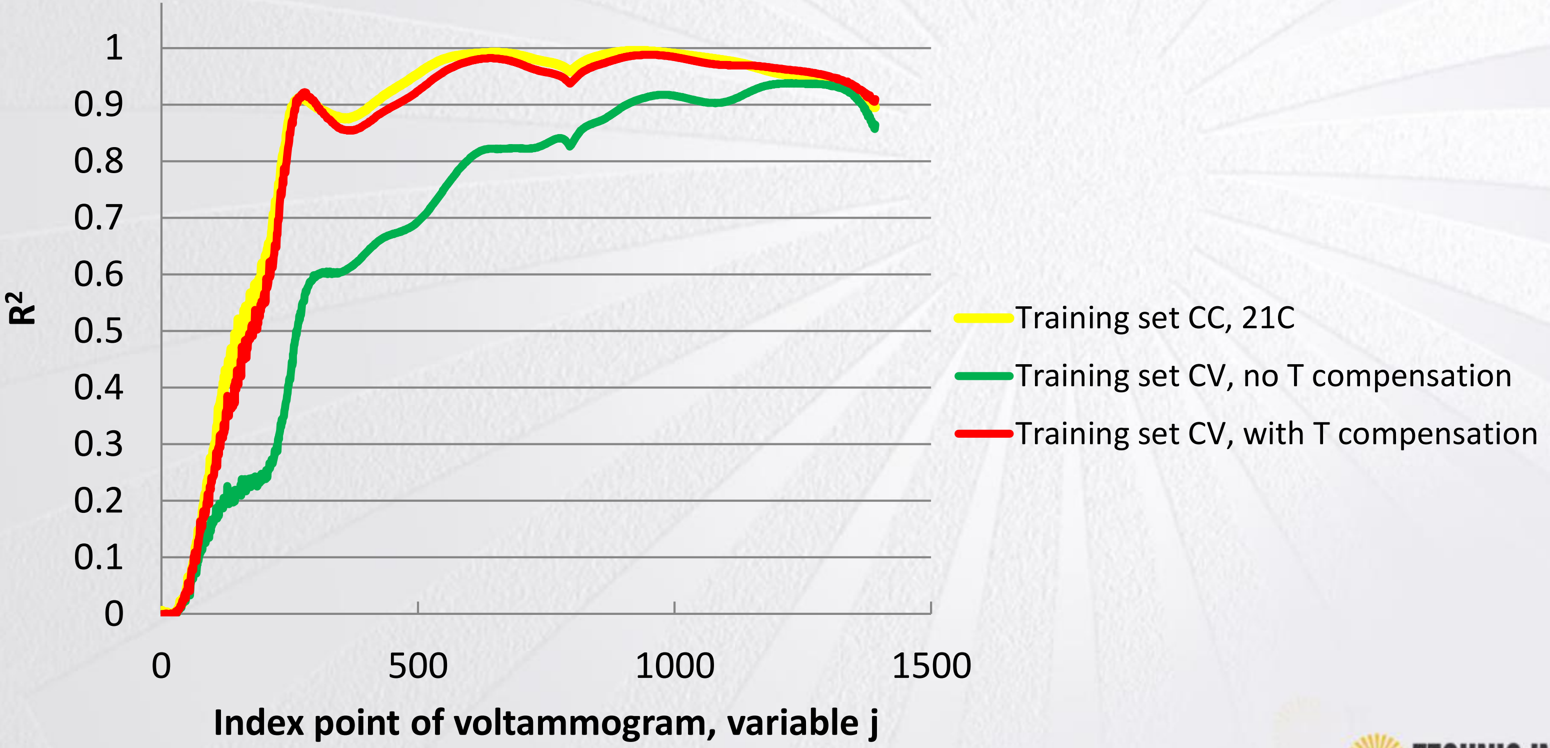
$\hat{c}_{i,j} = \beta_{0,j} + \beta_{1,j} x_{i,j}$	LSR equation
$\hat{c}_{i,j} = \beta_{0,j} + \beta_{1,j} x_{i,j} + \beta_{2,j} t_i$	trivariate regression eq.

$$R_j^2 = \frac{\left\{\sum_{i=1}^{I} c_i \hat{c}_{i,j} - \sum_{i=1}^{I} c_i \sum_{i=1}^{I} \hat{c}_{i,j}/I\right\}^2}{\left\{\sum_{i=1}^{I} c_i^2 - \left(\sum_{i=1}^{I} c_i\right)^2/I\right\}\left\{\sum_{i=1}^{I} \hat{c}_{i,j}^2 - \left(\sum_{i=1}^{I} \hat{c}_{i,j}\right)^2/I\right\}}$$

squared correlation coefficient

Variable Selection Based on Leveler Impact

Leveler calibrations: R^2 calculated individually for points of voltammograms of training sets CC and CV



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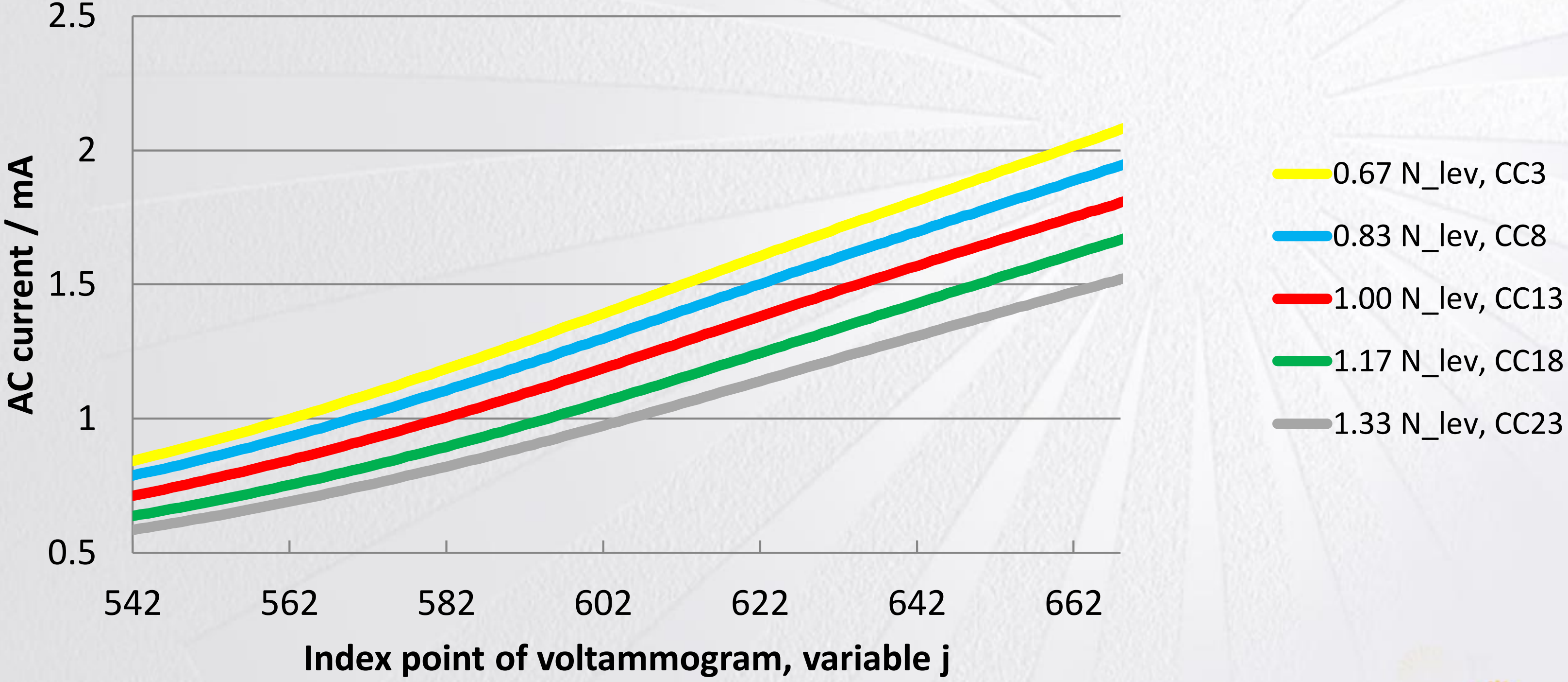
Variable Selection Based on Leveler Impact

A selected portion of AC voltammogram for a range corresponding to applied DC potential of 260 to 134 mV vs. E $_{Cu^{2+}/Cu}$, respectively recorded at 21°C for different concentrations of leveler additive.



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Variable Selection Based on Temperature Impact

Five subsets of the training set with parametrized leveler concentration

Leveler, N_{Lev}	Suppressor, N_{Supp}	Accelerator, N_{Acc}	Temperature °C
0.67	0.50	0.67	19.0
0.67	1.50	0.83	20.0
0.67	1.25	1.00	21.0
0.67	1.00	1.17	22.0
0.67	0.75	1.33	23.0
0.83	1.00	1.33	19.0
0.83	0.75	0.67	20.0
0.83	0.50	0.83	21.0
0.83	1.50	1.00	22.0
0.83	1.25	1.17	23.0
1.00	1.50	1.17	19.0
1.00	1.25	1.33	20.0
1.00	1.00	0.67	21.0
1.00	0.75	0.83	22.0
1.00	0.50	1.00	23.0
1.17	0.75	1.00	19.0
1.17	0.50	1.17	20.0
1.17	1.50	1.33	21.0
1.17	1.25	0.67	22.0
1.17	1.00	0.83	23.0
1.33	1.25	0.83	19.0
1.33	1.00	1.00	20.0
1.33	0.75	1.17	21.0
1.33	0.50	1.33	22.0
1.33	1.50	0.67	23.0

Variable Selection Based on Temperature Impact

Relationship between temperature and univariate voltammetric data within 1/5 subsets of the training set

$$\hat{t}_i = \alpha_{0,j} + \alpha_{1,j} x_{i,j}$$

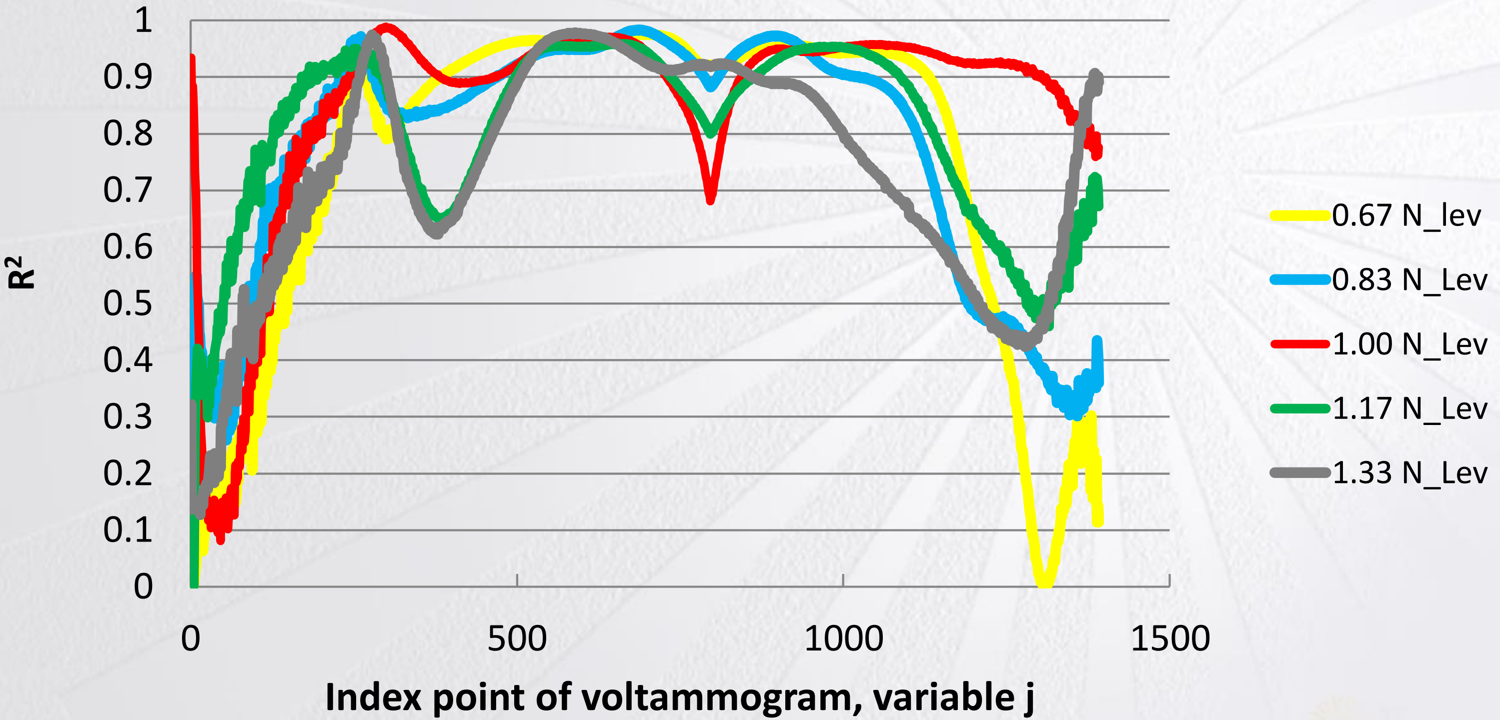
regression equation

$$R_{t,j}^2 = \frac{\left\{\sum_{i=1}^{I/5} t_i \hat{t}_{i,j} - \sum_{i=1}^{I/5} t_i \sum_{i=1}^{I/5} \hat{t}_{i,j} / (I/5)\right\}}{\left\{\sum_{i=1}^{I/5} t_i^2 - \left(\sum_{i=1}^{I/5} t_i\right)^2 / (I/5)\right\}\left\{\sum_{i=1}^{I/5} \hat{t}_{i,j}^2 - \left(\sum_{i=1}^{I/5} \hat{t}_{i,j}\right)^2 / (I/5)\right\}}$$

squared correlation coefficient

Variable Selection Based on Temperature Impact

Squared correlation coefficients between selfpredicted and actual temperature values calculated individually for each point of voltammogram, subsets of matrix CV with parametrized leveler concentration



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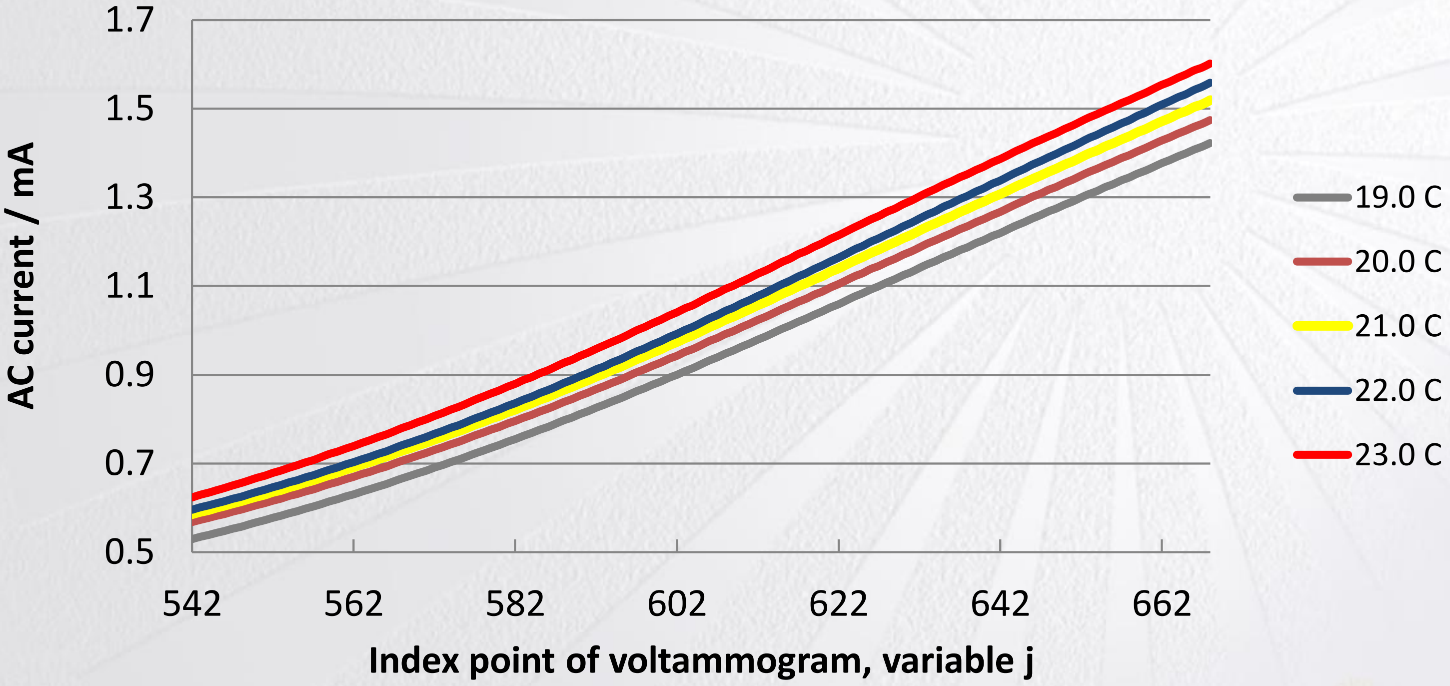
Variable Selection Based on Temperature Impact

AC voltammogram for leveler, selected range 542-668, dependence on temperature at parametrized leveler concentration of 1.33 N_Lev



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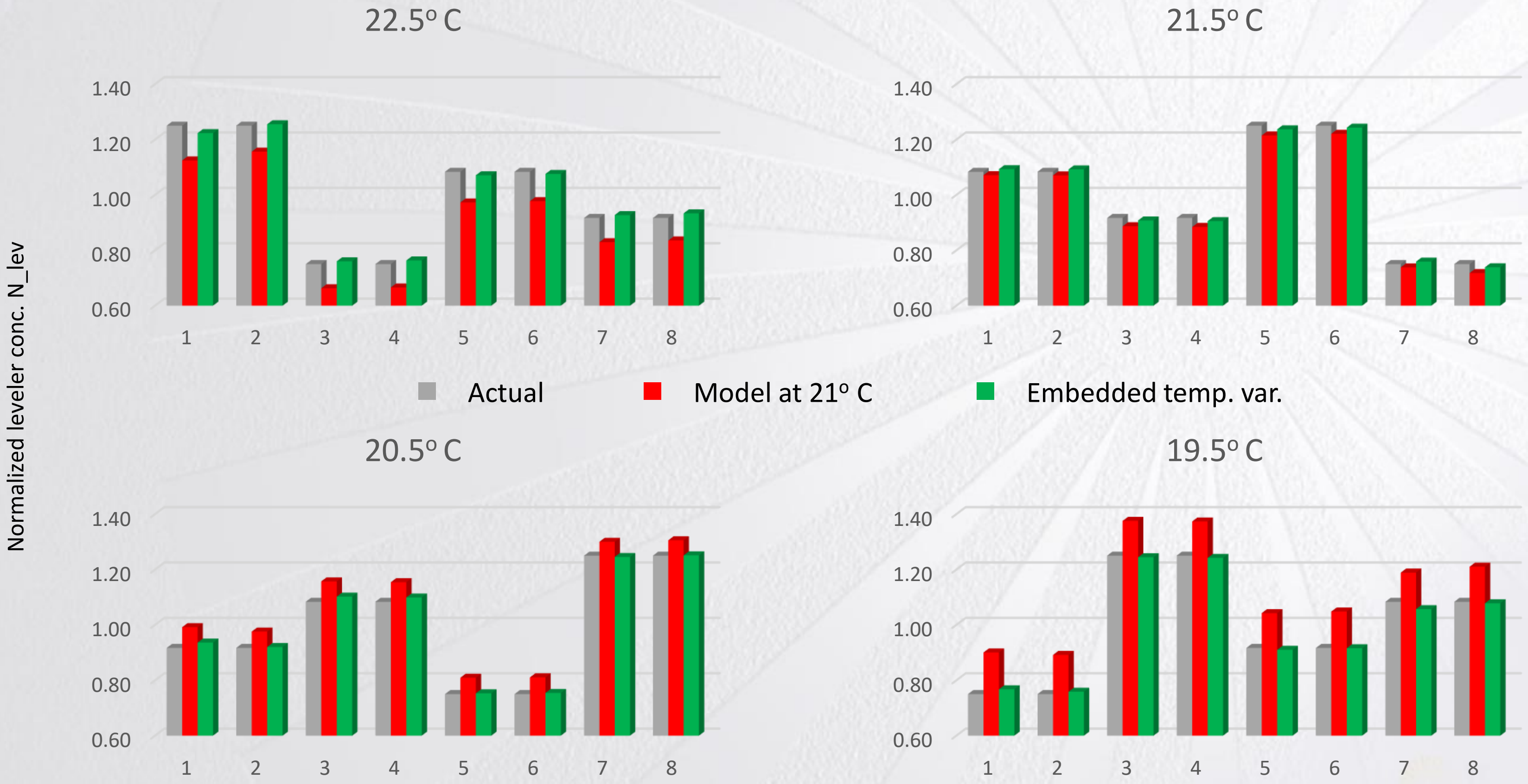
Calibration Calculation by Principal Component Regression (PCR)

$\boldsymbol{X} = \boldsymbol{S}\boldsymbol{V}^T + \boldsymbol{E}$	PCA decomposition into scores $\boldsymbol{S}$ and loadings $\boldsymbol{V}$
$\boldsymbol{\beta} = (\boldsymbol{S}^T\boldsymbol{S})^{-1}\boldsymbol{S}^T\boldsymbol{c}$	Inverse Least Squares Regression on scores
$\hat{c}_u = \boldsymbol{x}_u\boldsymbol{V}\boldsymbol{\beta}$	Regression equation
$\boldsymbol{S}_t = [\boldsymbol{S}\ \boldsymbol{t}]$	PCA scores augmented with temperature
$\boldsymbol{\beta}_t = (\boldsymbol{S}_t^T\boldsymbol{S}_t)^{-1}\boldsymbol{S}_t^T\boldsymbol{c}$	Inverse Least Squares Regression on scores augmented with temperature
$\hat{c}_u = [\boldsymbol{x}_u\boldsymbol{V}\ t_u]\boldsymbol{\beta}_t$	Regression equation with embedded temperature variance

Prediction of Leveler Concentration in Validation Set Samples



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Conclusions

General, rigorous routine for the development of the analytical method using a chemometric model with temperature variation embedded in regression is introduced for exemplary determination of leveler additive concentration by AC voltammetry.

Chemometrics is critical in mitigating the adverse effect of temperature variation on accuracy of concentration prediction by an on-line AC voltammetric analyzer.

Accurate calibration can be calculated for experimental conditions where hard-models do not exist.

Chemometrics promotes an interest in AC-based electroanalytical techniques for industrial applications.