

**Model formulation and interpretation  
for chemical reactions mechanisms  
- from experiment to theory**

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From kinetics study of a given pair of reactants different types of mechanisms were investigated. A mathematical model was formulated. Model parameters were evaluated and assessed. Obtained results from the optimization procedure opened an interesting discussion about the limits of parameters obtained from experiments data for imposed conditions, such as mechanism type and collecting procedure.

By using of a least squares method, obtained models as best fits correlates with experimental measurements; the results shown an average of 96.6% for a sample size average of 2967 pairs of data.

Comparing the results obtained by different experiments, all obtained parameters, which were not related with the experimental conditions, were in same range of 95% confidence interval. These results validates experimental data and as well as data obtained by model.

# **Model formulation and interpretation for chemical reactions mechanisms - from experiment to theory**

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# Introduction

- Mathematical modeling of reaction kinetics are necessary when we want to identify a supposed chemical mechanism [Piotr PIETRZYK, Barbara GIL, Zbigniew SOJKA: Combining computational and in situ spectroscopies joint with molecular modeling for determination of reaction intermediates of deNO<sub>x</sub> process-CuZSM-5 catalyst case study, Catalysis Today, 126(1-2), 2007, 103-111]
- Kinetic-based methods are using in determination of various substances, as chlorine and oxychlorine species [Gordon G, Yoshino K, Themelis DG, Wood D, Pacey GE: Utilisation of kinetic-based flow injection methods for the determination of chlorine and oxychlorine species, Anal Chim Acta, 224, 1989, 383-390] and GPT activity in human serum [He Y-N, Chen H-Y: The kinetics-based electrochemical determination of serum glutamate pyruvate transaminase activity with a gold microelectrode, Anal Chim Acta, 353, 1997, 319-323]

# Motivation & aim

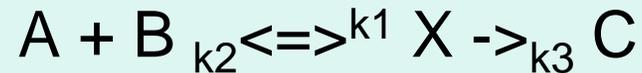
- Starting with a previous experience in optimization of processes [Cimpoiu C, Jäntschi L, Hodisan T: A New Mathematical Model for the Optimization of the Mobile Phase Composition in HPTLC and the Comparison with Other Models, J Liq Chromatogr Related Technol, 22, 1999, 1429-1441], an optimization procedure which can be used in order to validate a chemical mechanism by using a modified partial least squares method has been developed and their consistency are discussed here.
- The algorithm were run on large measured sample data and it's ability to identify parameters of chemical interest such as reaction partially and globally rates and orders were proved.

# Materials

- Measured extinction values depending on time served as input data in our model. The data were measured on a stopped-flow installation build at Technical University of Cluj-Napoca [Mihaela - Ligia ABRUDEAN c. UNGUREȘAN: Reacții redox rapide de reducere ale ionilor Cu (II) cu tiocombinații, PhD Thesis (Gavril NIAC PhD Advisor), defended on 3 Jul 2007 at Babes-Bolyai University of Cluj-Napoca].
- Reactants were cooper and tiosulfate. Three sample data was available, for extinction time of the intermediary of the reaction when reactants were prepared in same concentration: 1 (1100 data pairs), 5 (1300), and 10 (6500) mM. The data were measured with a baud rate of 0.04 ms at wavelength of 430 nm.

# Reaction kinetics

- The kinetics of reaction between copper and tiosulfate were supposed to be of following type:



- The associated reaction rates are:

$$v = k_1[A]^{y_1}[B]^{y_2}$$

$$v = k_2[X]^{y_3}$$

$$v = k_3[X]^{y_4}$$

where  $[A]$ ,  $[B]$ , and  $[X]$  are the instant concentration of chemicals,  $k_j$ ,  $j = 1..3$  rates constants, and  $y_i$ ,  $i = 1..4$  partial orders.

- In order to fit the theoretical mechanism with measured data, another two physical laws were implied: mass conservation and Lambert-Beer.

# Mathematical equations

- The reaction rate is typically of the form:

$$dX/dt = k_1[A]^{y_1}[B]^{y_2} - k_2[X]^{y_3} - k_3[X]^{y_4}$$

- where:

$$[A] = [A]_0 - k_1[A]^{y_1}[B]^{y_2}dt + k_2[X]^{y_3}dt$$

$$[B] = [B]_0 - k_1[A]^{y_1}[B]^{y_2}dt + k_2[X]^{y_3}dt$$

$$[X] = [X]_0 + (k_1[A]^{y_1}[B]^{y_2}dt - k_2[X]^{y_3}dt - k_3[X]^{y_4}dt)$$

- Differencing and renouncing at brackets:

$$dA = -k_1A^{y_1}B^{y_2}dt + k_2X^{y_3}dt$$

$$dB = -k_1A^{y_1}B^{y_2}dt + k_2X^{y_3}dt$$

$$dX = (k_1A^{y_1}B^{y_2} - k_2X^{y_3} - k_3X^{y_4})dt$$

- More:

$$dA/A = -k_1Bdt, \quad dB/B = -k_1Adt$$

# Numerical equations

- Passing the derivatives to finite differences, we have:

$$A_i = A_{i-1} - k_1 A_{i-1}^{y1} B_{i-1}^{y2} dt + k_2 X_{i-1}^{y3} dt$$

$$B_i = B_{i-1} - k_1 A_{i-1}^{y1} B_{i-1}^{y2} dt + k_1 X_{i-1}^{y3} dt$$

$$X_i = X_{i-1} - (k_1 A_{i-1}^{y1} B_{i-1}^{y2} - k_2 X_{i-1}^{y3} - k_3 X_{i-1}^{y4}) dt$$

- Let's note with  $D_{i-1}$  the following expression:

- $D_{i-1} = k_1 A_{i-1}^{y1} B_{i-1}^{y2} - k_2 X_{i-1}^{y3}$

- Using this, the above equations become:

$$A_i = A_{i-1} - D_{i-1} dt$$

$$B_i = B_{i-1} - D_{i-1} dt$$

$$X_i = X_{i-1} + (D_{i-1} - k_2 X_{i-1}^{y3}) dt$$

- Starting conditions - characterized by:  $A_0=B_0$  and  $X_0=0$

# Model data

- Following was input data independent of experiment:
  - $dt = 4 \cdot 10^{-5}$  – baud rate (seconds);
  - $X_0 = 0$  – initial concentration of intermediary (moles);
- Following was input data dependent of experiment:
  - $A_0=B_0=1;5;10$  - initial concentrations of reactants (mili-moles);
  - $N=1100;1300;6500$  (pairs of time-extinction measurements);
- Regression:
  - Equation:  $\hat{E} = a \cdot X + b$ ,  $\hat{E}$  estimator of Extinction
  - Loss function:  $S = M(E^2) + M^2(XE) - 2M^2(XE)/M(X^2)$

# Optimization procedure

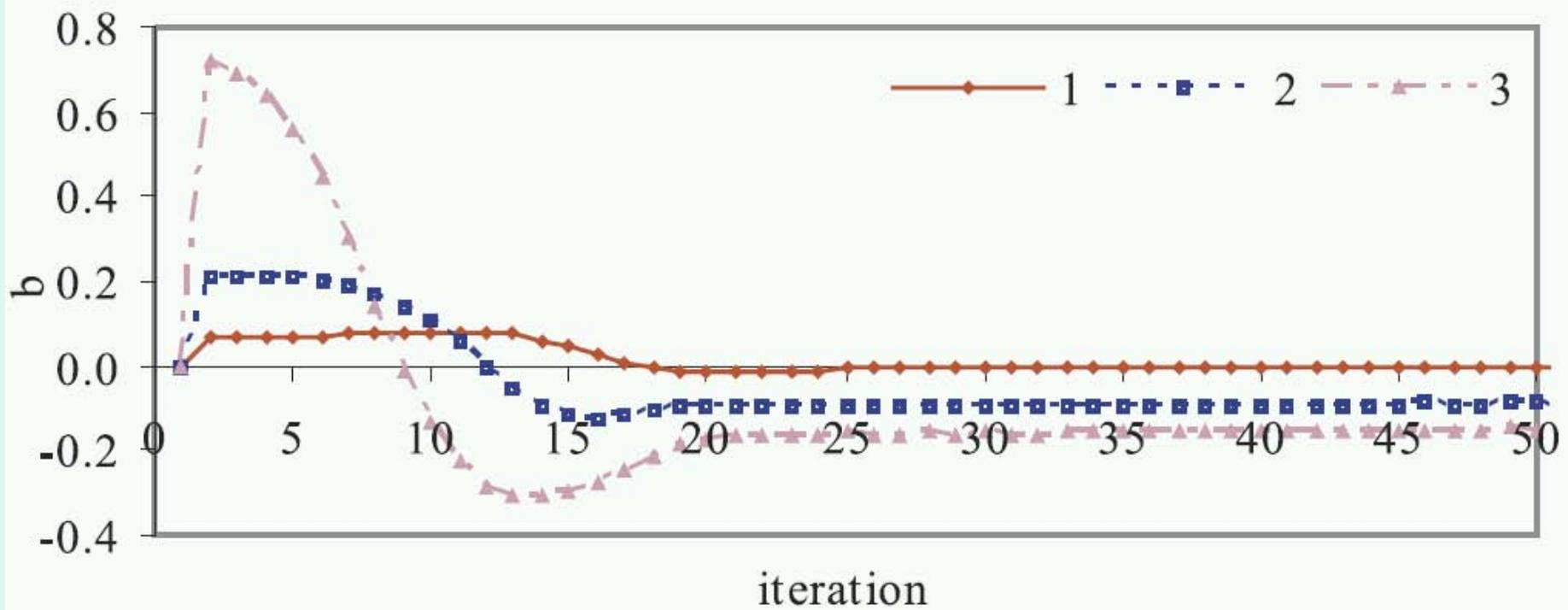
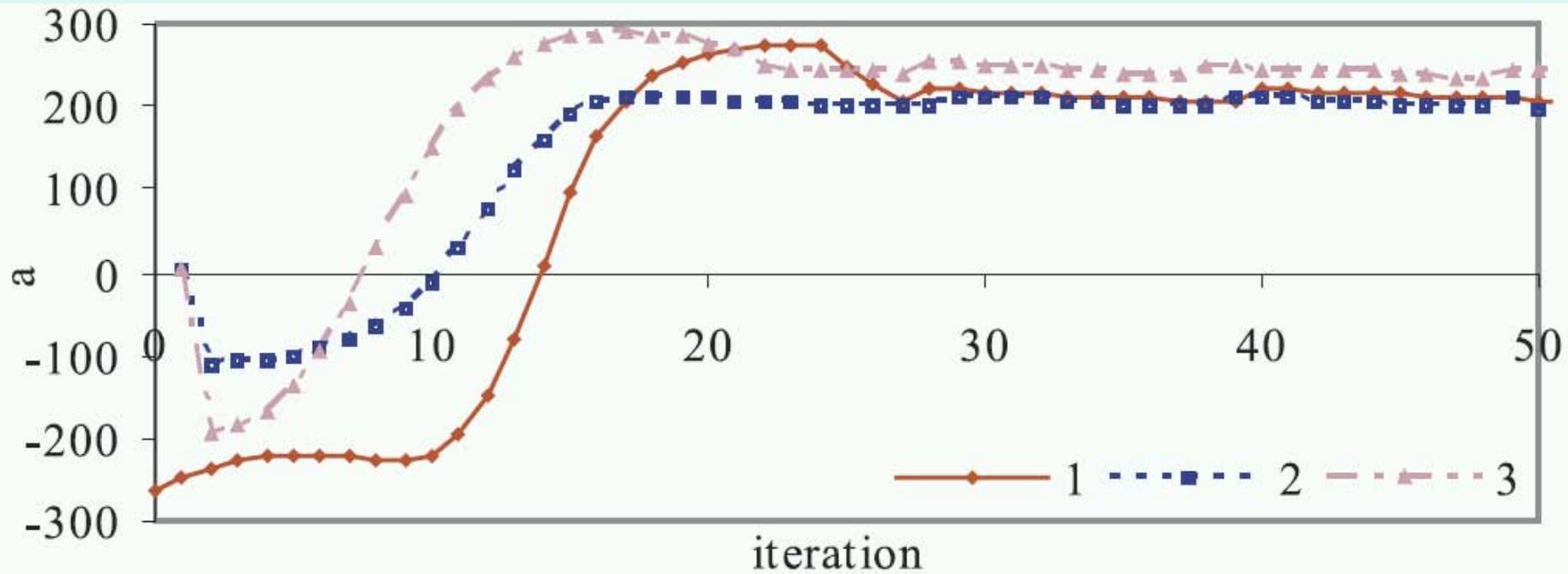
- Our model has following:
- Targeted variables:
  - $k_1, k_2, k_3$  – rates constants;
  - $y_1, y_2, y_3, y_4$  – partial orders;
- True variables:
  - $a$  (contains extinction coefficient);
  - $b$  (record the displacing of recording from initial moment,  $t = 0$ );
- $S = S(X, E) \Rightarrow S = S(k_1, k_2, k_3, y_1, y_2, y_3, y_4, a, b) = \min$
- Let  $\text{diff}$  be a small relative variation ( $\text{diff}$  was set to 1%); for each targeted variable a small relative variation was made (for  $k_1$ :  $0.99 \cdot k_1, 1.00 \cdot k_1, 1.01 \cdot k_1$ ). When all variables vary, a number of  $3^7$  different series of values were obtained; for each series, the quality factor  $S$  was calculated.

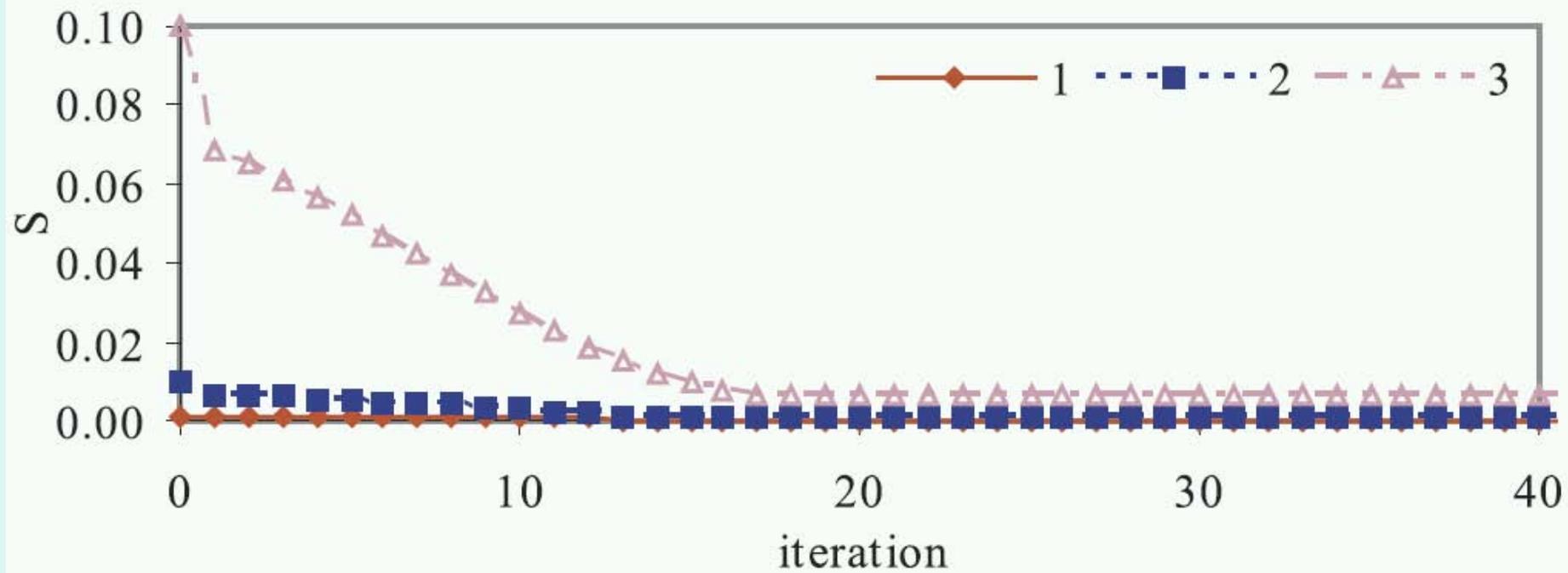
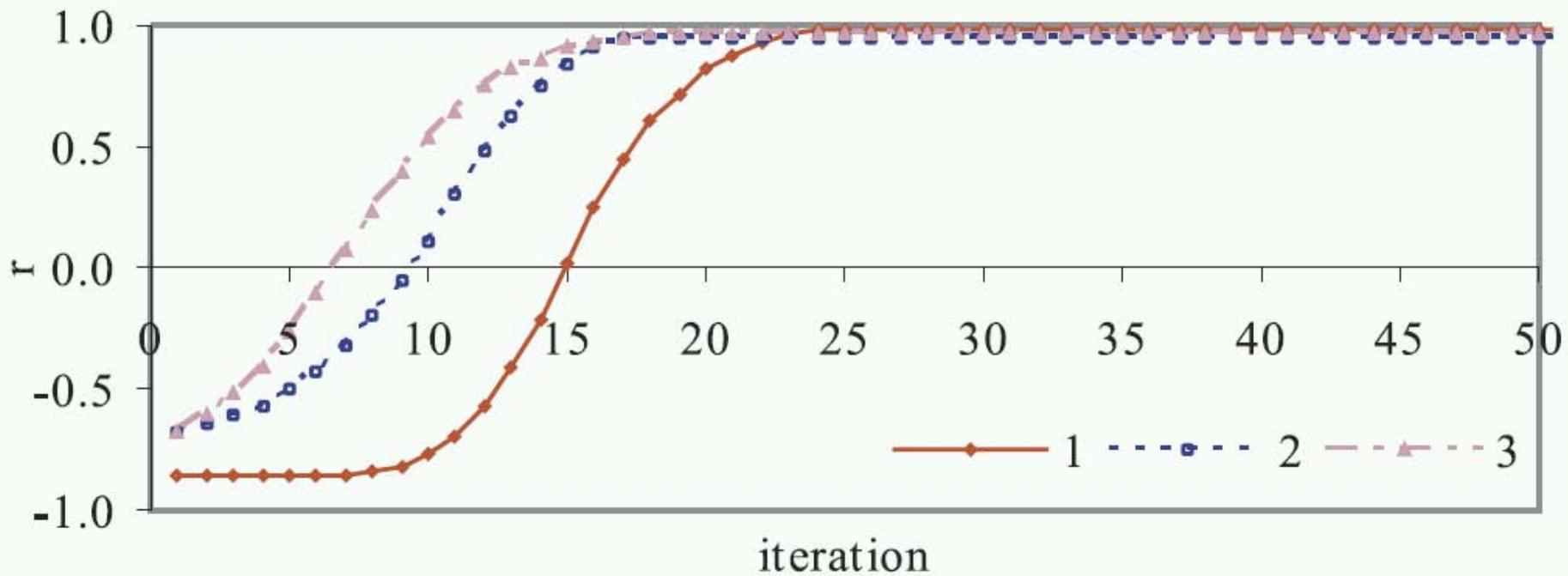
# Optimization constrains

- Algorithm advances on iterating based on the minimum of quality factor  $S$  selected from all  $3^7$  values computed at one iteration. The optimum process was considered when the method convergences towards credible results, and the optimized values of variable become almost constant.
- Following criteria were imposed:
  - minimum residual error  $S$ ;
  - valid reaction rates (nonnegative, acceptable range);
- Note that the reaction between copper (II) and tiosulfate ions is very fast, measurements being difficult to do. Some authors appreciate that the reaction time is close to or below detection limit, thus only in part the measured data has reliability.

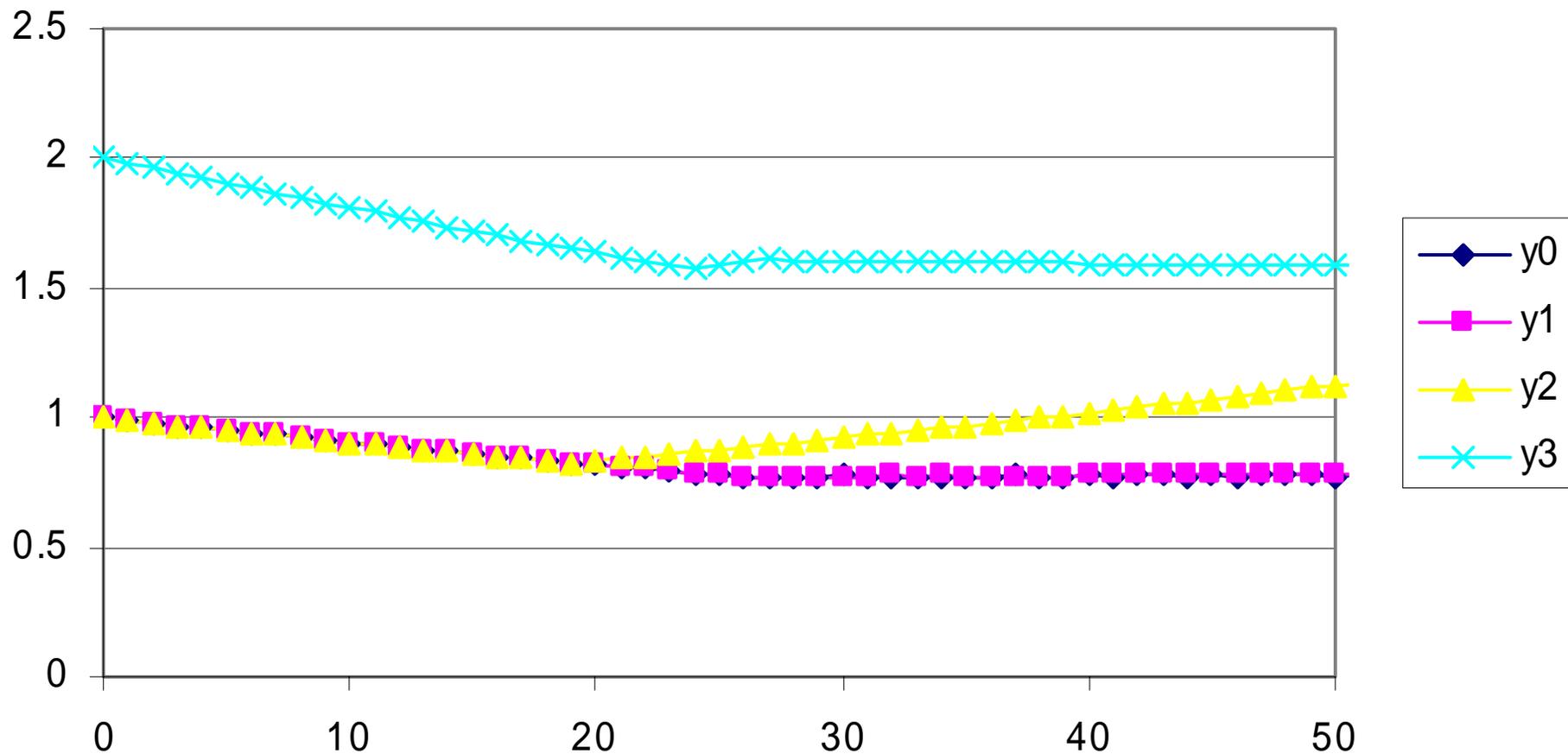
# Optimization results

- The model parameters values fits one to each other to 95% confidence intervals for all three experimental data sets.
- Only the first part of the experimental data were relevant and entered into the optimization procedure (1100 for 0.001 M, 1300 for 0.005 M, and 6500 for 0.01M).
- Obtained results are in table 1, where  $a$  and  $b$  are coefficients of the regression equation  $\hat{E} = aX + b$ . The dependence of the regression coefficients  $a$  and  $b$ ,
- correlation coefficient  $r$  and residues sum  $S$  depending on iteration step are in next figure.

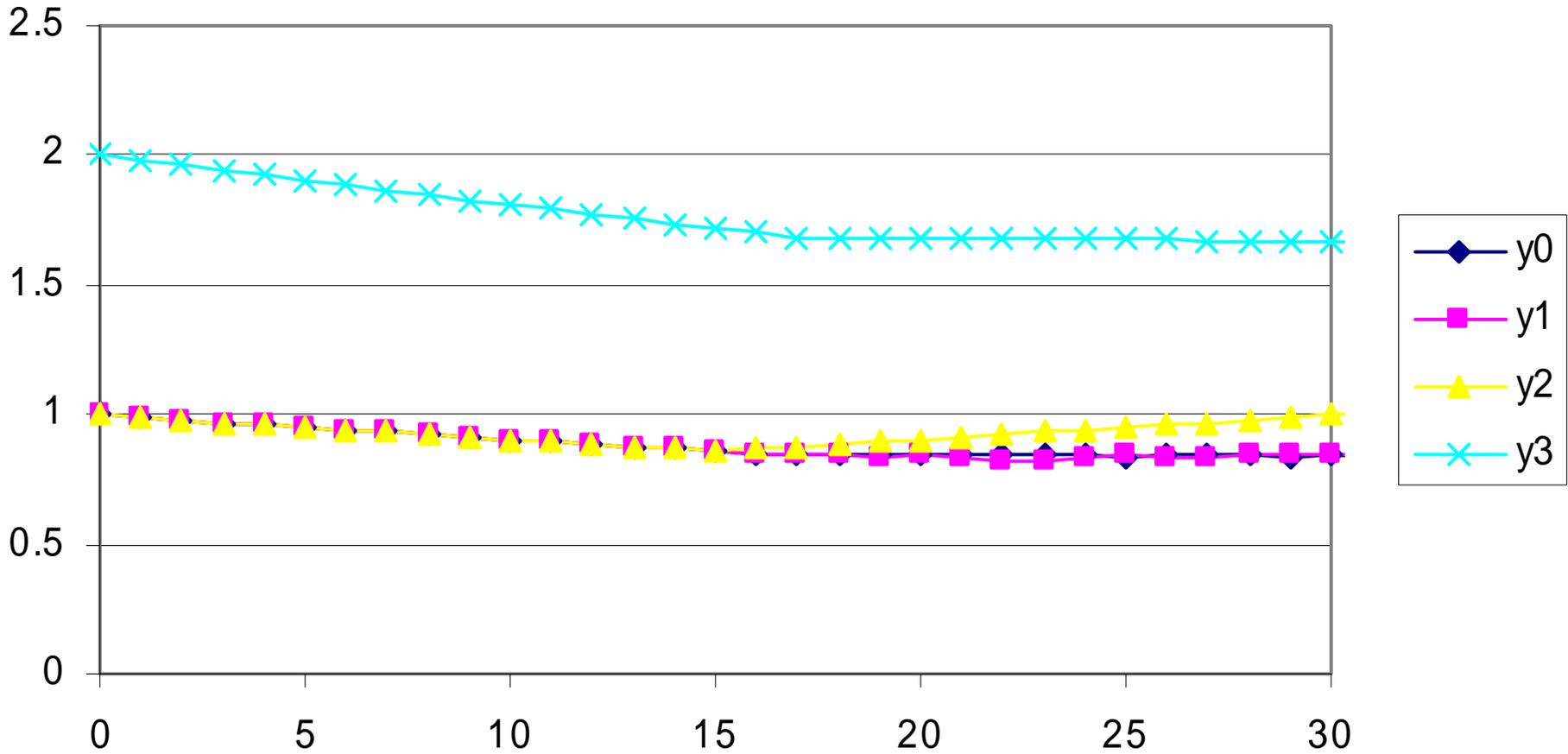




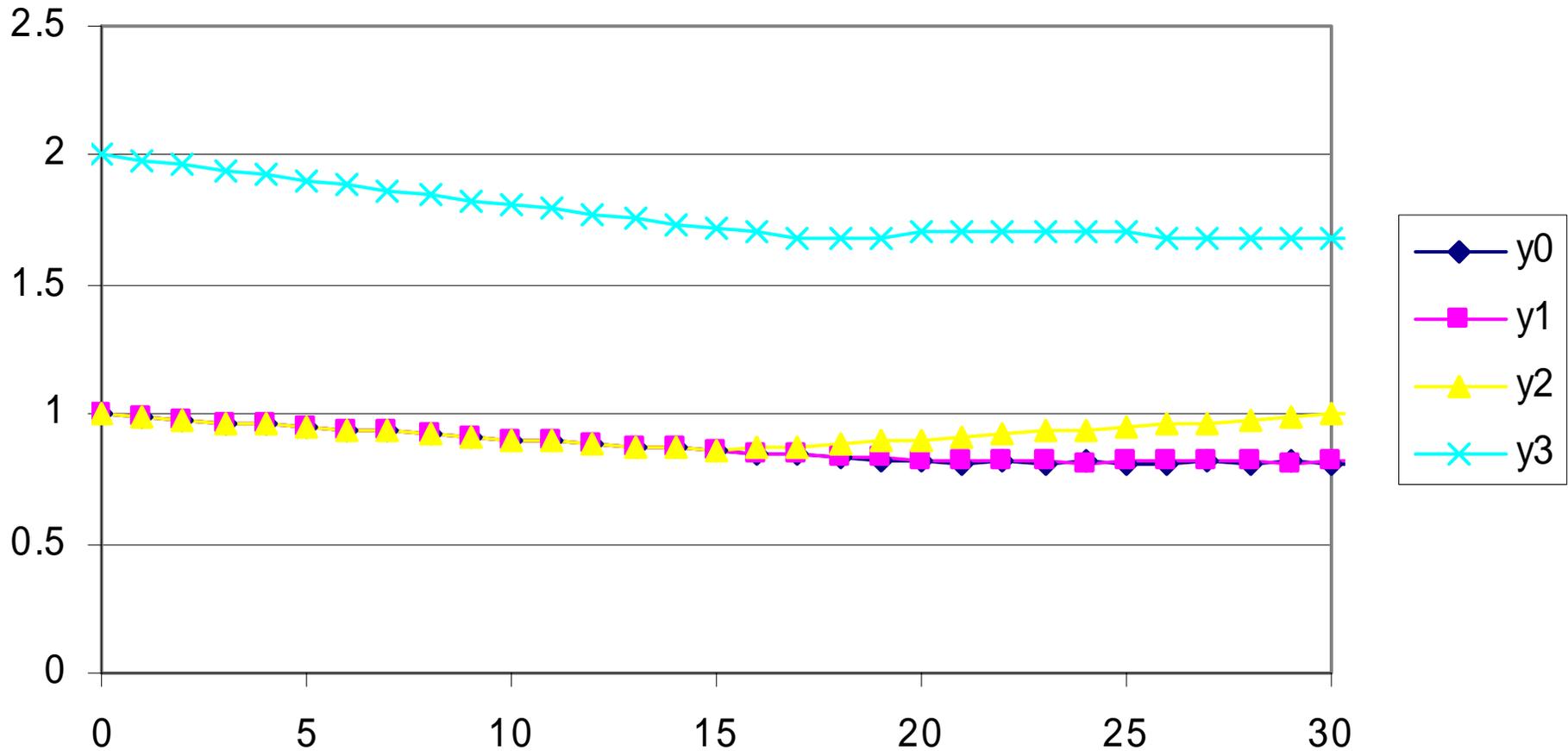
# Partial orders for 1 mM (y2 not reliable)



# Partial orders for 5 mM (y2 not reliable)



# Partial orders for 5 mM (y2 not reliable)



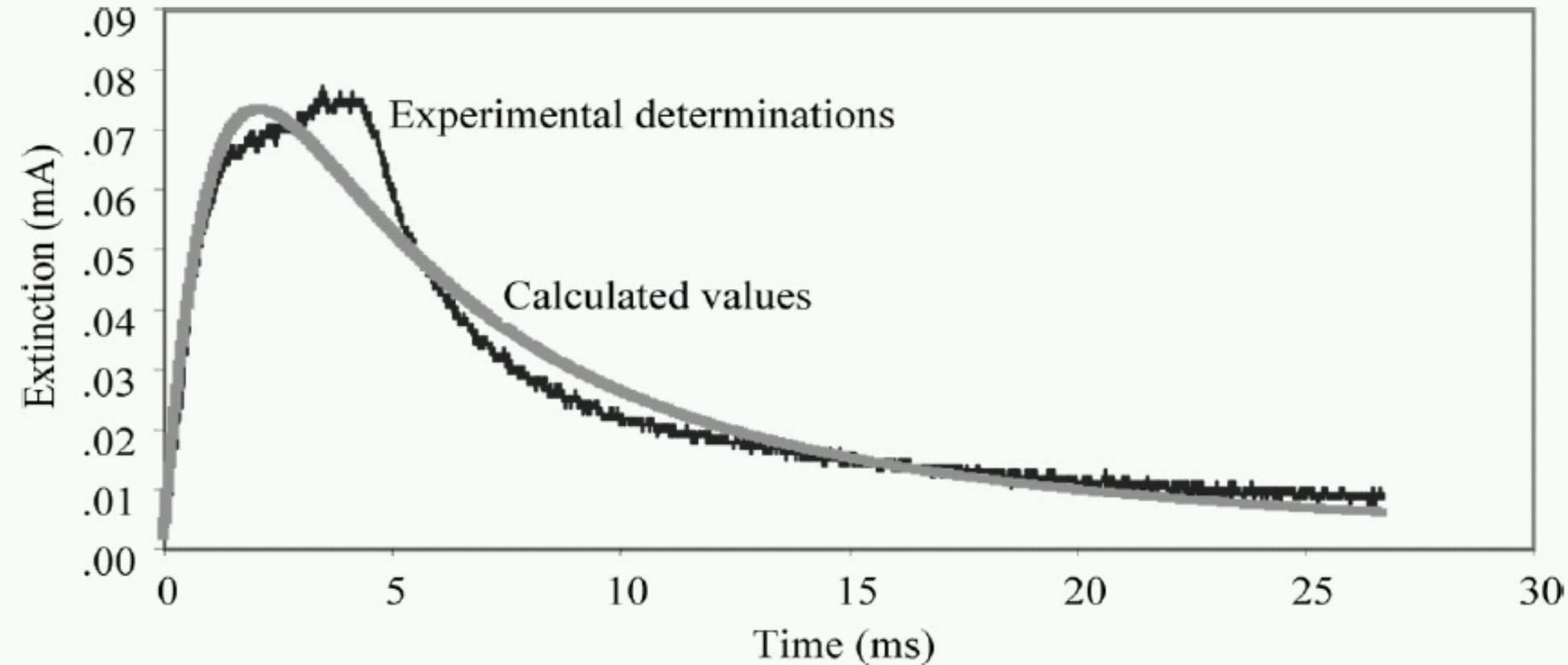
# Optimized parameters

E	$y_0$	$y_1$	$y_3$	$k_0$	$k_2$	$S$	$C_0$	$a$	$b$	$r$	$IS$
1	0.82	0.81	1.51	3.46	2.30	1.81	1	219	-0.0005	0.980	107
2	0.80	0.79	1.57	1.02	2.04	66.6	5	189	-0.0821	0.955	99
3	0.75	0.75	1.57	0.82	2.10	582	10	227	-0.1300	0.962	99

E - experiment no;  $y_0$  to  $y_3$  - partial orders;  $k_0, k_2$  - rates ( $\cdot 10^3$ );  $y_2, k_1$  - not reliable; S - residue ( $\cdot 10^{-5}$ );  $\hat{E} = aX+b$ ; r - correlation coefficient; IS = Iteration Step;  $C_0 = [A_0]=[B_0]$  (mMoles)

# Experiment vs. theory

- On the following were given the experimental results from 1-st experiment against all three pairs of obtained parameters from previous table (all calculated superposes)



# Conclusions

- The obtained results are far to be perfect; but proposed optimization method is converging towards credible results for the reaction: partial orders and rates into error limits, credible variance of the constants.
- The certainties are the values of the partial orders, rates and constants, values that stabilized with iteration. Neither the proposed method of calculus nor experimental determinations were rigorous.
- Note that, being a fast reaction, biases can appear easy in collecting of the experimental determinations.
- The proposed mathematical model proved to be rapid and versatile optimization method.

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