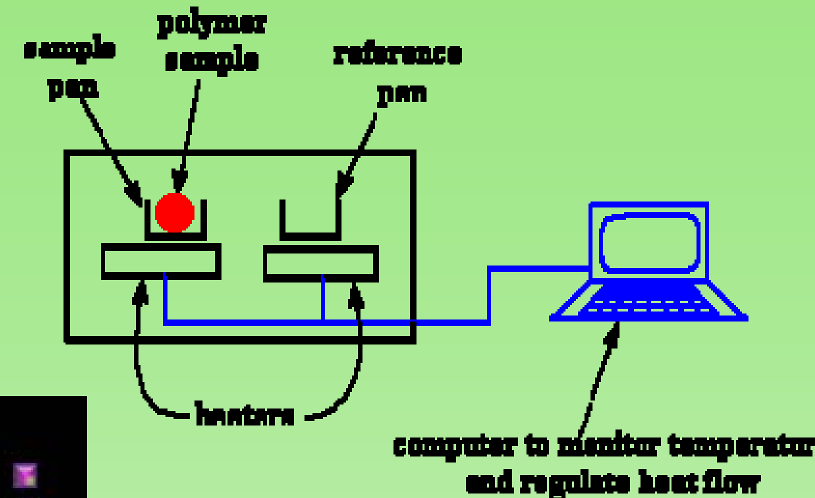
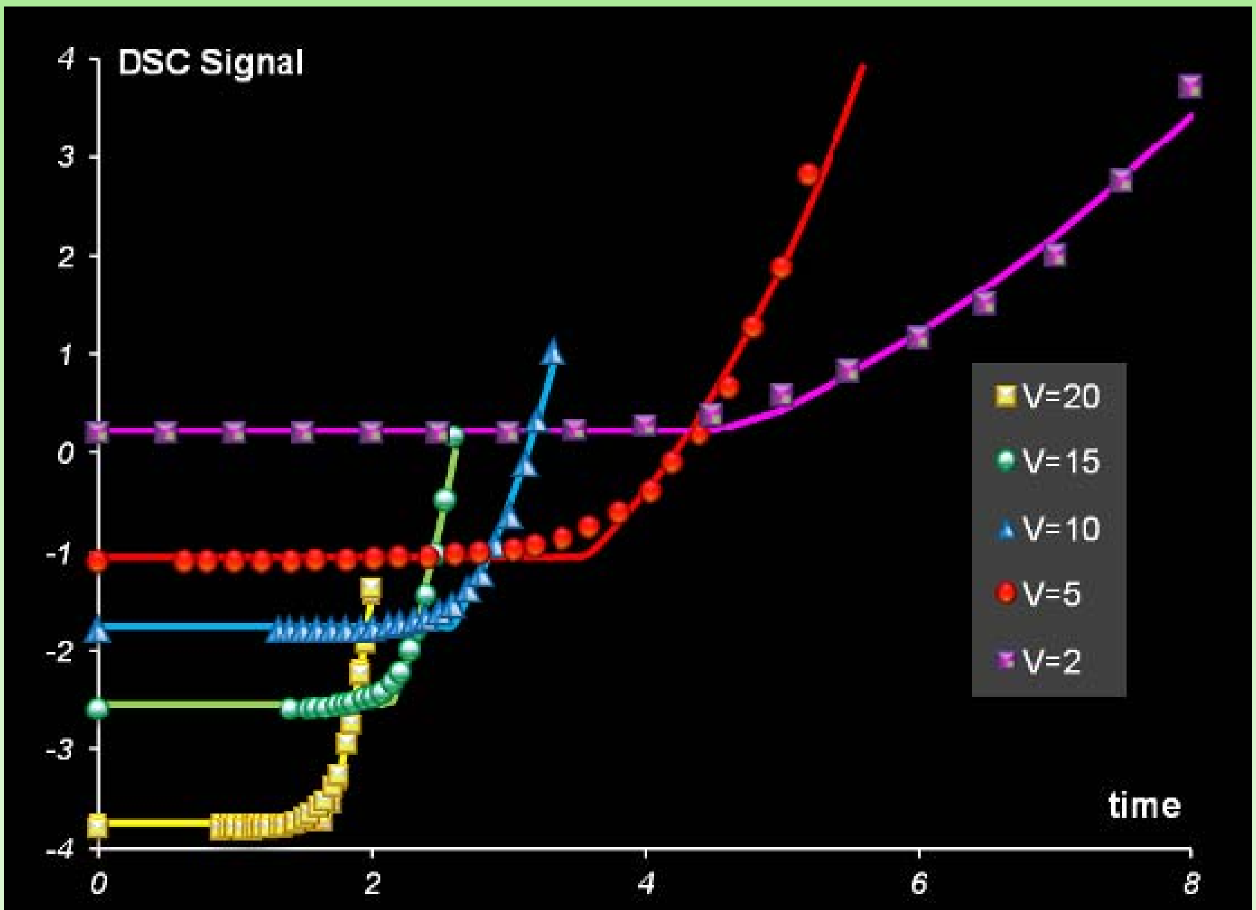
Successive Bayesian Estimation as a tool for chemometric modelling of kinetic data

Alexey Pomerantsev

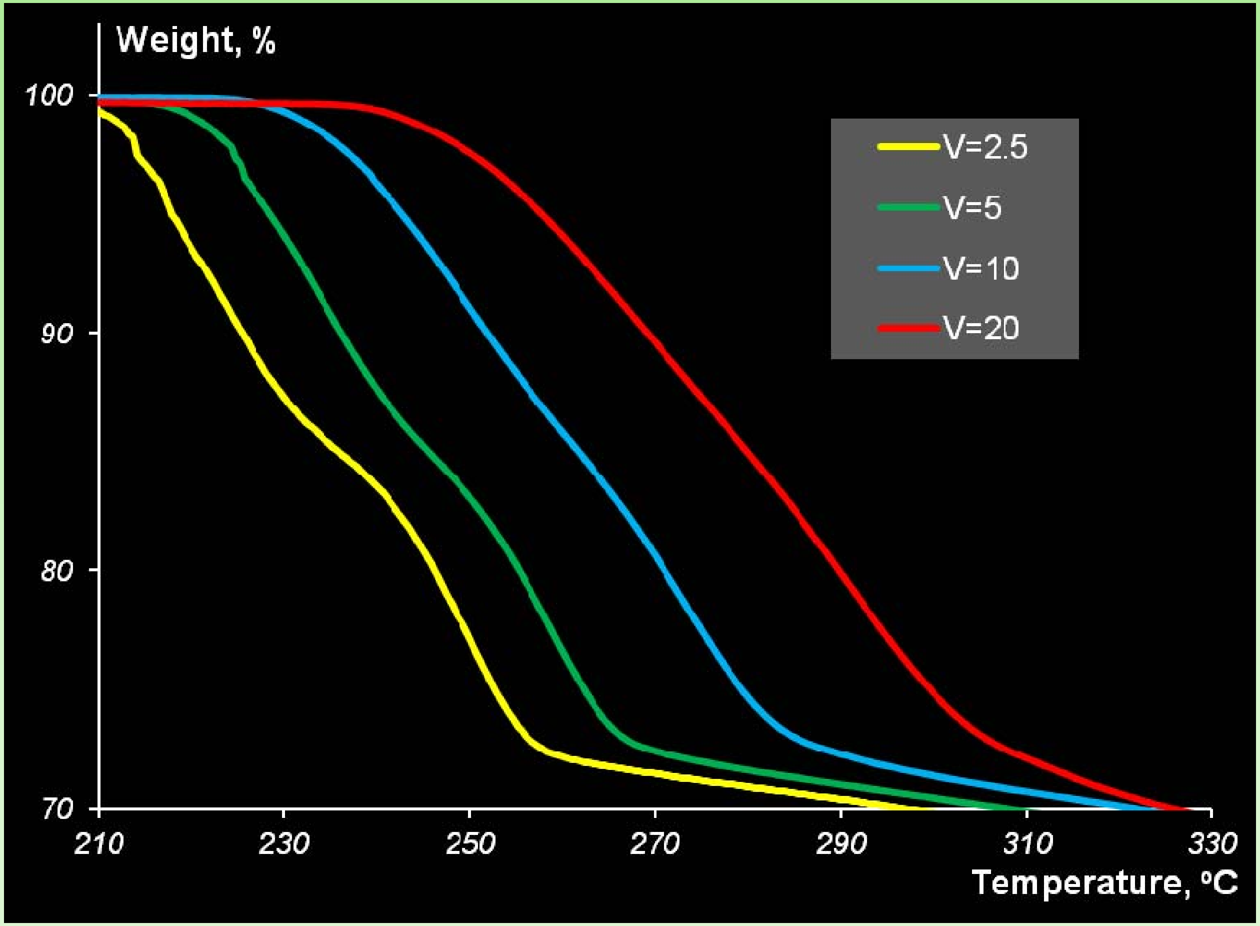
Semenov Institute of Chemical Physics
Russian Chemometrics Society

DSC data

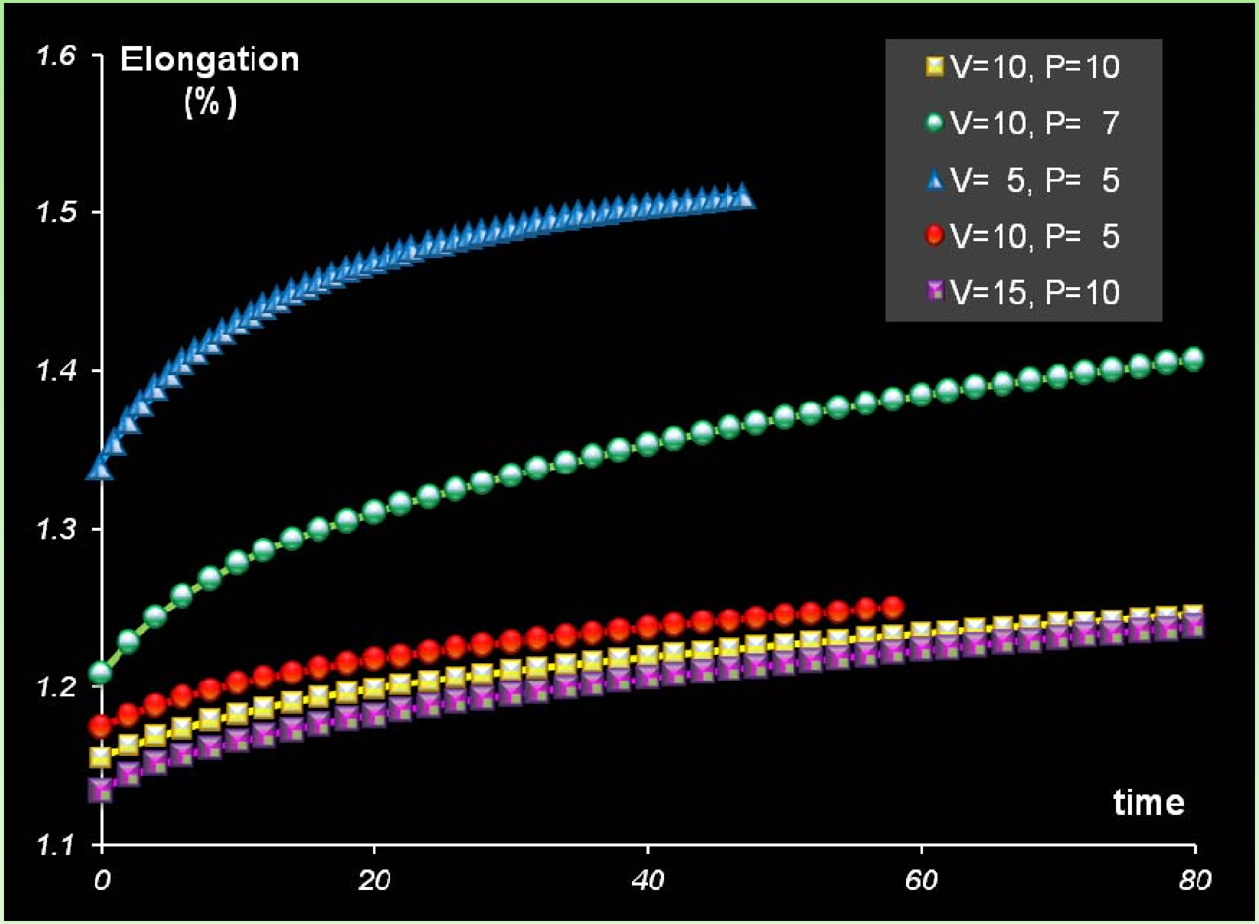

sample pan
polymer sample
reference pan
heaters
computer to monitor temperature and regulate heat flow

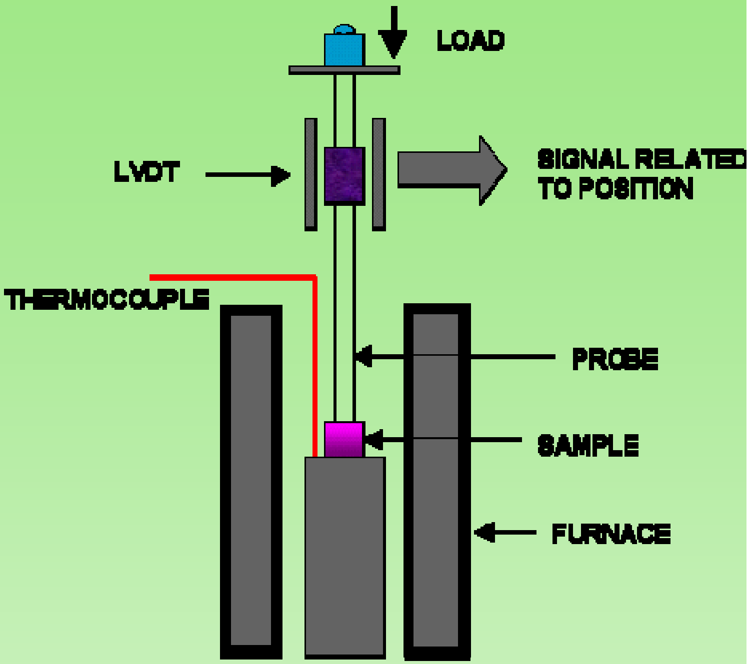

DSC Signal
time
V=20
V=15
V=10
V=5
V=2
4
3
2
1
0
-1
-2
-3
-4
0
2
4
6
8

TGA Data

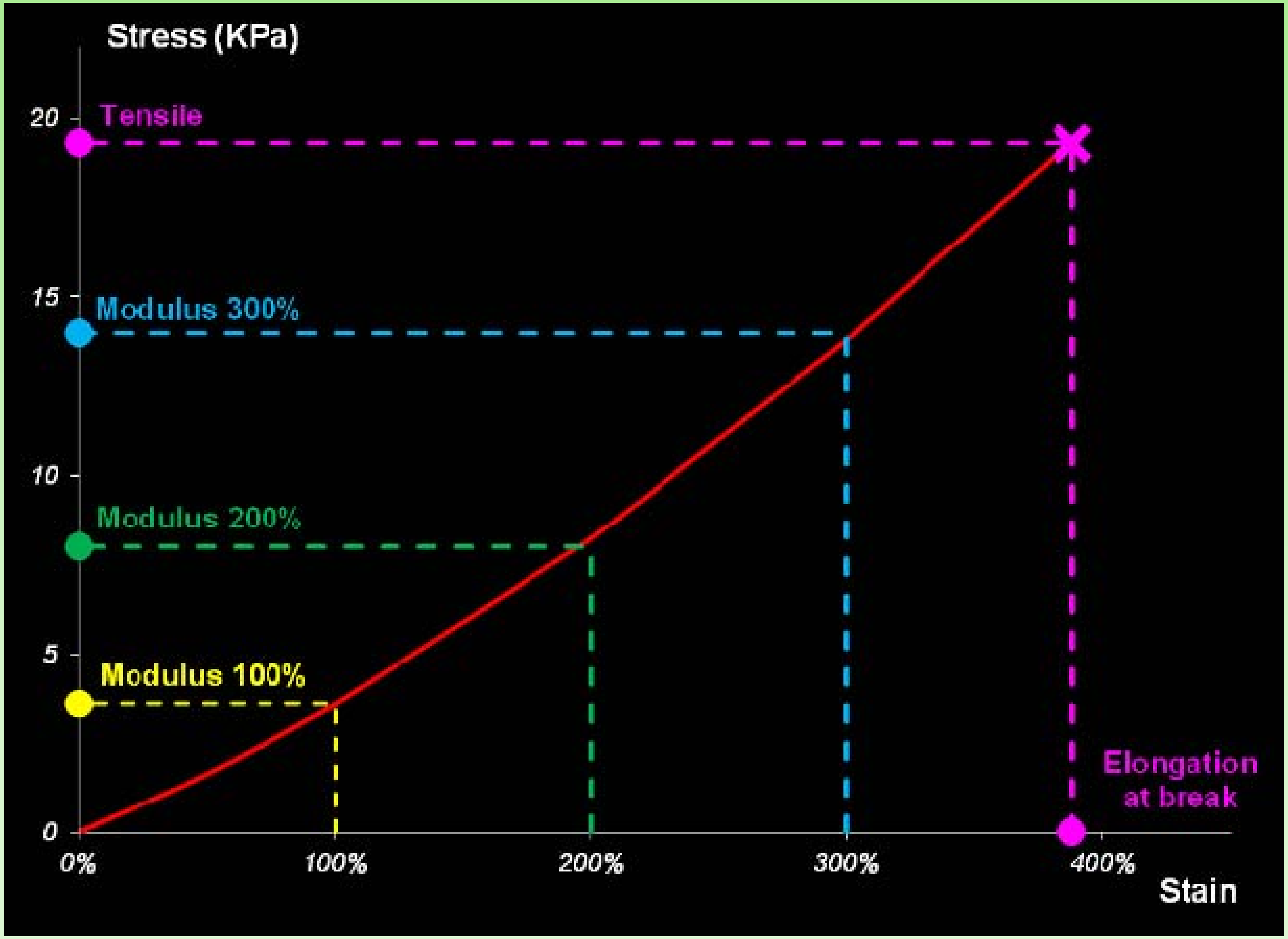

Weight, %
100
90
80
70
V=2.5
V=5
V=10
V=20
210
230
250
270
290
310
330
Temperature, ºC

TMA data

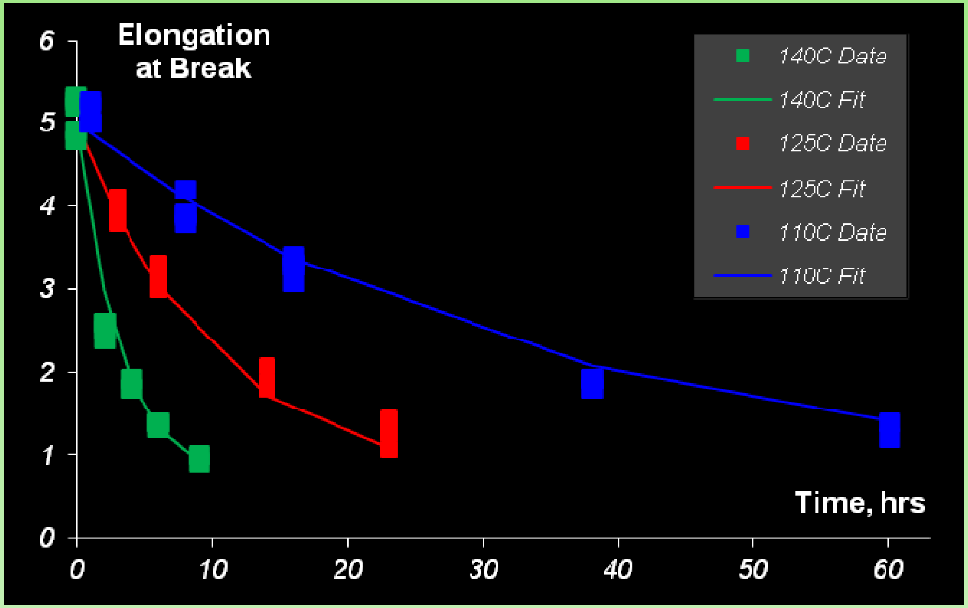

Elongation
(%)
V=10, P=10
V=10, P= 7
V= 5, P= 5
V=10, P= 5
V=15, P=10
time
1.6
1.5
1.4
1.3
1.2
1.1
0
20
40
60
80

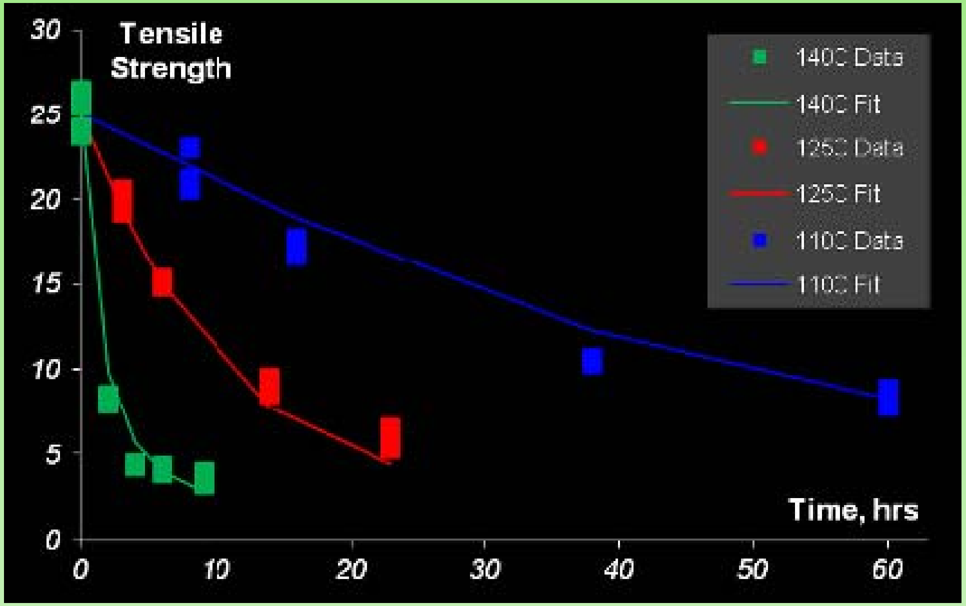

LOAD
LVDT
SIGNAL RELATED TO POSITION
THERMOCOUPLE
PROBE
SAMPLE
FURNACE

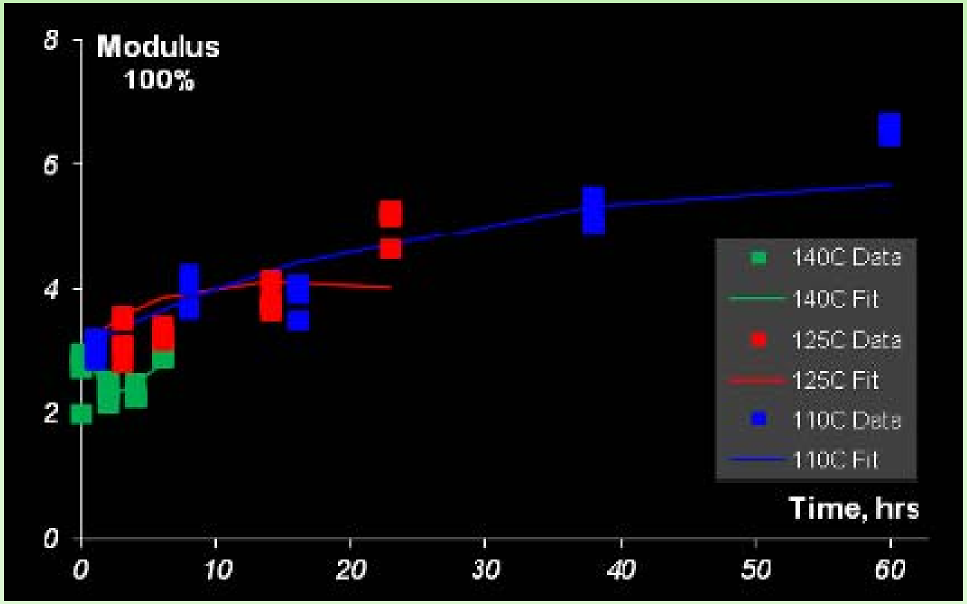
Stress–strain experiment

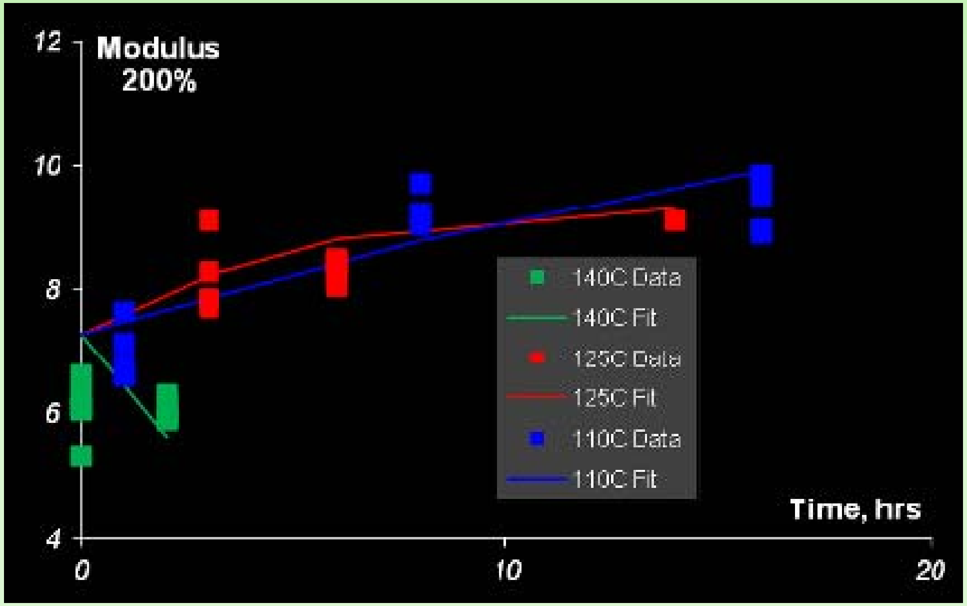


Stress–strain data









Data Structure

Elongation @ Break

$110^{O}C$
$125^{O}C$
$140^{O}C$

Tensile

$110^{O}C$
$125^{O}C$
$140^{O}C$

Modulus 100%

$110^{O}C$
$125^{O}C$
$140^{O}C$

Modulus 200%

$110^{O}C$
$125^{O}C$
$140^{O}C$

Modulus 300%

$110^{O}C$
$125^{O}C$
$140^{O}C$

Modulus 400%

$110^{O}C$
$125^{O}C$
$140^{O}C$

Modulus 500%

$110^{O}C$
$125^{O}C$
$140^{O}C$

Models structure

- 3×7 data blocks = 21 models

- each model depends on m parameters

  $f\,(t,T \mid a_1,a_2,\ldots,a_m) \qquad m \approx 7$

- $3 \times 7 \times m \approx 150$ parameters to estimate

- some are common, e.g. Arrhenius' parameters:

  $a = k\exp(E/\mathrm{R}/T)$

- finally:

7 models, 8 partial and 4 common parameters

OLS & SBE for two blocks

OLS

$$\mathbf{y} = \mathbf{y}_1 \otimes \mathbf{y}_2 \qquad \mathbf{f}(\mathbf{a}) = \mathbf{f}_1(\mathbf{a}) \otimes \mathbf{f}_2(\mathbf{a})$$

$$S(\mathbf{a}) = \left\| \mathbf{y} - \mathbf{f}(\mathbf{a}) \right\|^2 = S_1(\mathbf{a}) + S_2(\mathbf{a}) = \left\| \mathbf{y}_1 - \mathbf{f}_1(\mathbf{a}) \right\|^2 + \left\| \mathbf{y}_2 - \mathbf{f}_2(\mathbf{a}) \right\|^2$$

$$\hat{\mathbf{a}}_{\mathrm{OLS}} = \arg\min_{\mathbf{a}} S(\mathbf{a})$$

SBE

$$\hat{\mathbf{a}}_1 = \arg\min_{\mathbf{a}} S_1(\mathbf{a}) \qquad S_1(\mathbf{a}) \approx S_1(\hat{\mathbf{a}}_1) + (\mathbf{a} - \hat{\mathbf{a}}_1)^{\mathbf{t}} \mathbf{A} (\mathbf{a} - \hat{\mathbf{a}}_1) = B(\mathbf{a})$$

$$S(\mathbf{a}) \approx Q(\mathbf{a}) = S_2(\mathbf{a}) + B(\mathbf{a})$$

$$\hat{\mathbf{a}}_{\mathrm{SBE}} = \arg\min_{\mathbf{a}} Q(\mathbf{a})$$

Likelihood approach

$$L(\mathbf{a},\sigma^2) = \mathrm{Const}\,\sigma^{-(N_1+N_2)} \exp\left(-\frac{S_1(\mathbf{a}) + S_2(\mathbf{a})}{2\sigma^2} \right)$$

$$S_i(\mathbf{a}) = \left\| \mathbf{y}_i - \mathbf{f}_i(\mathbf{a}) \right\|^2, \quad i = 1,2$$

$$L(\mathbf{a},\sigma^2) = \mathrm{Const}\,\sigma^{-(N_1+N_2-2)} \exp\left(-\frac{B_1(\mathbf{a}) + S_2(\mathbf{a})}{2\sigma^2} \right)$$

$$B_1(\mathbf{a}) = N_1 s_1^2 + (\mathbf{a} - \hat{\mathbf{a}}_1)^{\mathbf{t}} \mathbf{A} (\mathbf{a} - \hat{\mathbf{a}}_1)$$

$$L(\mathbf{a},\sigma^2) = \mathrm{Const}\,\sigma^{-(N_1-2)} \exp\left(-\frac{B_1(\mathbf{a})}{2\sigma^2} \right) \times \sigma^{-N_2} \exp\left(-\frac{S_2(\mathbf{a})}{2\sigma^2} \right) =$$

$$= L_{\mathrm{Prior}}(\mathbf{a},\sigma^2) \times L_{\mathrm{Data}}(\mathbf{a},\sigma^2)$$

SBE procedure

1) Process first block alone

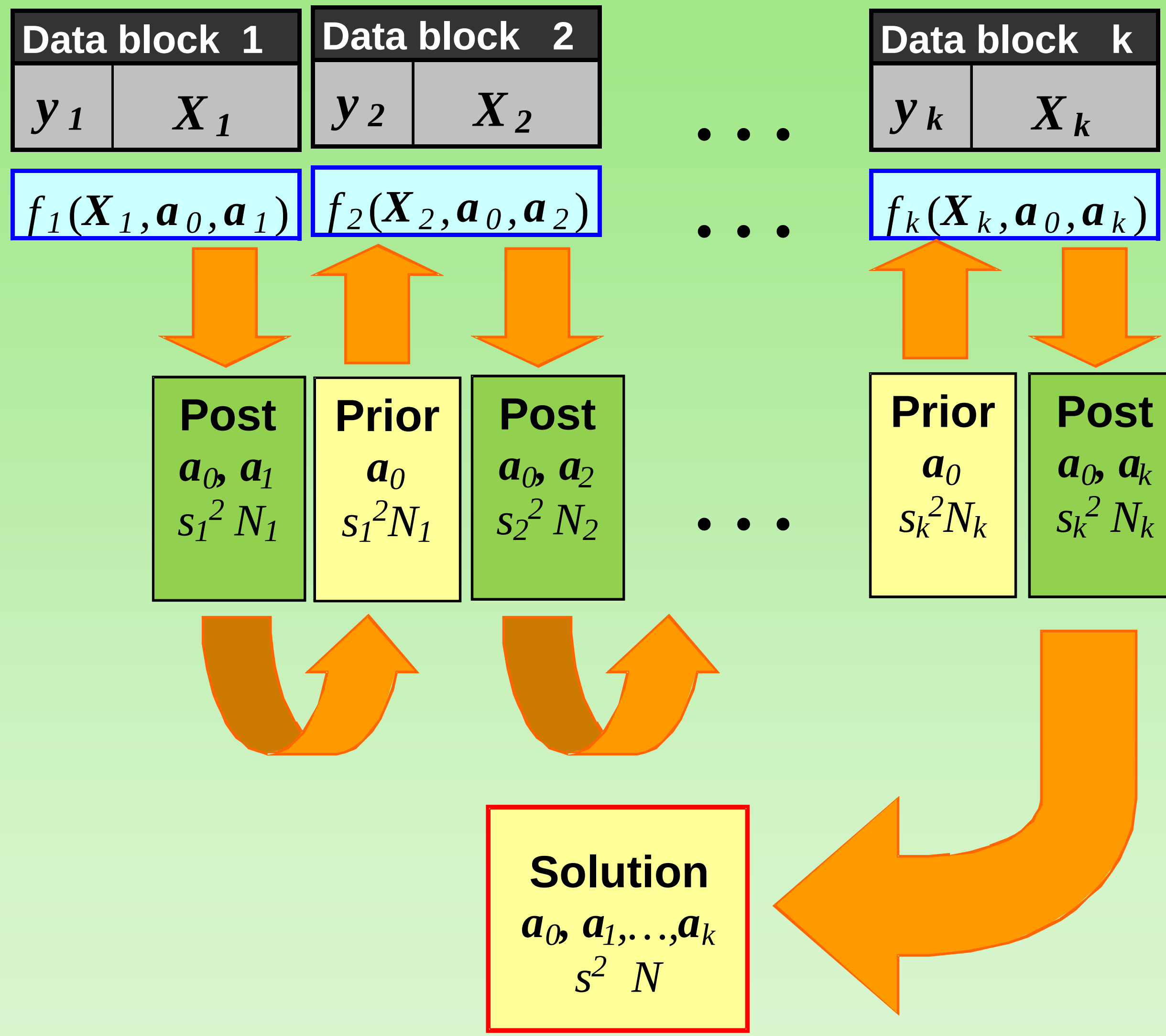
2) Make posterior information

3) Convert it to prior information

4) Use it for the next block

5) Repeat this for all blocks

6) Last result is the solution



Posterior & Prior Information

Block 1. Posterior Information

$$B_1(\mathbf{a}) = N_1\, s_1^2 + (\mathbf{a} - \widehat{\mathbf{a}}_1)^{\mathbf{t}}\, \mathbf{A}(\mathbf{a} - \widehat{\mathbf{a}}_1)$$

Rebuilding (common & partial parameters)

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}_{00} & \mathbf{A}_{01} \\ \mathbf{A}_{01}^{\mathrm{t}} & \mathbf{A}_{11} \end{bmatrix} \qquad \mathbf{H} = \begin{bmatrix} \mathbf{A}_{00} - \mathbf{A}_{01}\mathbf{A}_{11}^{-1}\mathbf{A}_{01}^{\mathrm{t}} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix}$$

$$\hat{\mathbf{a}}_1 = \begin{bmatrix} \hat{\mathbf{a}}_0 \\ \hat{\mathbf{a}}_{11} \end{bmatrix} \qquad \mathbf{b}_1 = \begin{bmatrix} \hat{\mathbf{a}}_0 \\ \mathbf{0} \end{bmatrix}$$

Block 2. Prior Information

$$B_2(\mathbf{a}) = N_1\, s_1^2 + (\mathbf{a} - \mathbf{b}_1)^{\mathrm{t}}\, \mathbf{H}(\mathbf{a} - \mathbf{b}_1)$$

SBE Main Theorem

Different order of blocks processing

$1 \rightarrow 2$

$$\widehat{\mathbf{a}}^{12}_{\mathrm{SBE}} = \arg\min_{\mathbf{a}}\left[S_2(\mathbf{a}) + B_1(\mathbf{a})\right]$$

$2 \rightarrow 1$

$$\widehat{\mathbf{a}}^{21}_{\mathrm{SBE}} = \arg\min_{\mathbf{a}}\left[S_1(\mathbf{a}) + B_2(\mathbf{a})\right]$$

Theorem (1995)

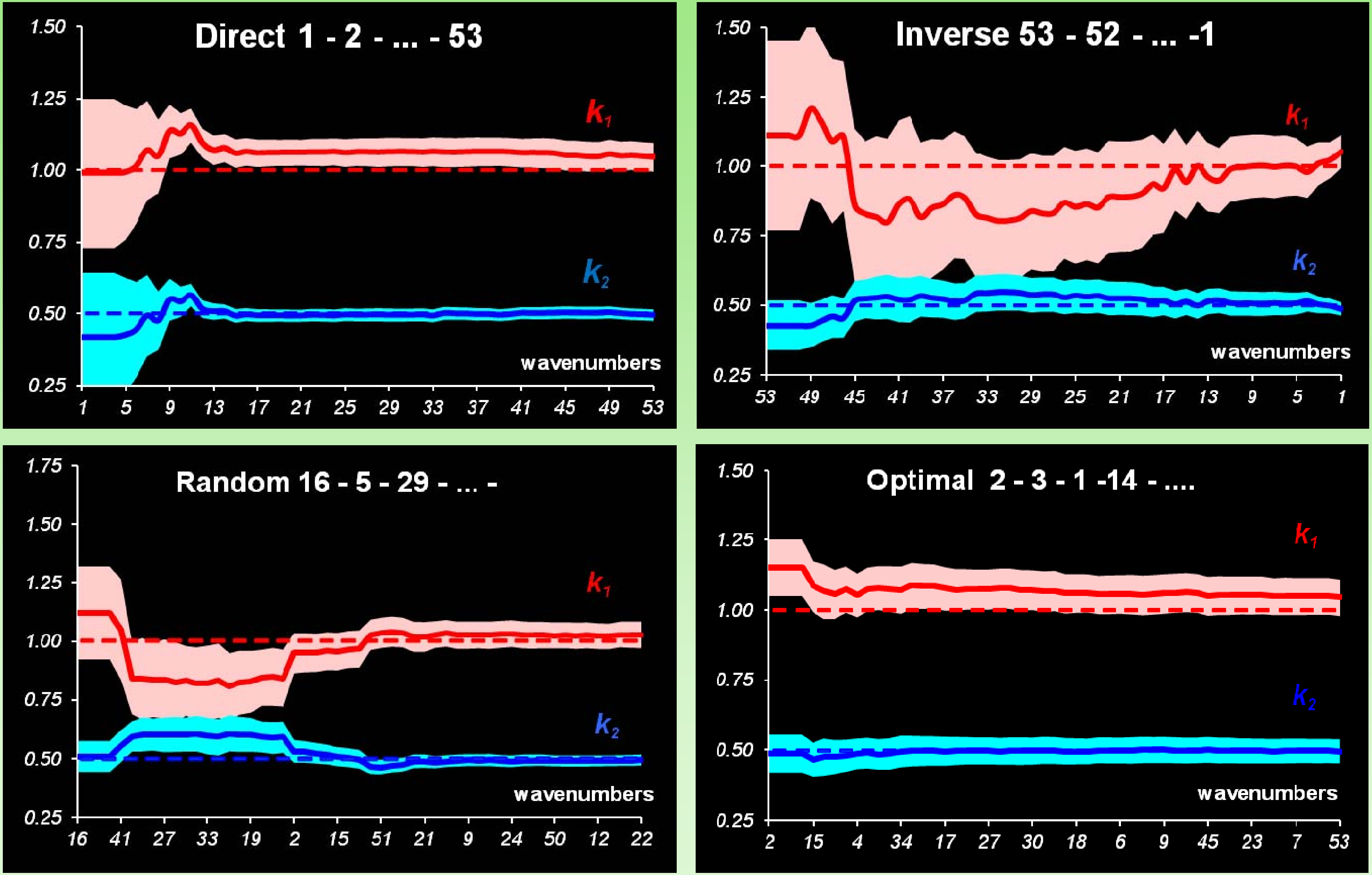
1) Linear regression

$$\widehat{\mathbf{a}}^{12}_{\mathrm{SBE}} = \widehat{\mathbf{a}}^{21}_{\mathrm{SBE}} = \widehat{\mathbf{a}}_{\mathrm{OLS}}$$

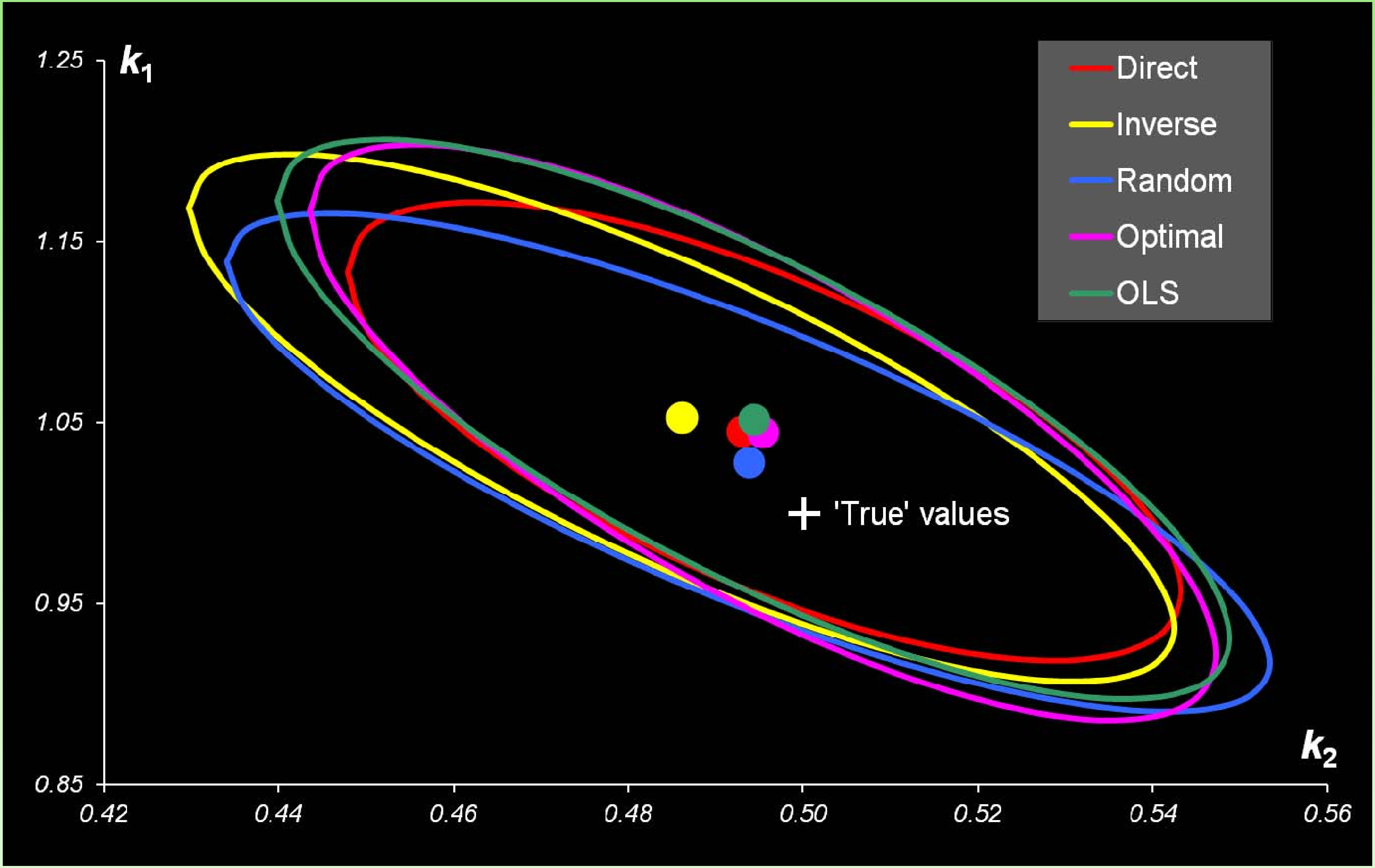
2) Nonlinear regression

$$\widehat{\mathbf{a}}^{12}_{\mathrm{SBE}} \rightarrow \widehat{\mathbf{a}}_{\mathrm{OLS}} \leftarrow \widehat{\mathbf{a}}^{21}_{\mathrm{SBE}} \quad \text{at } N \rightarrow \infty$$

Example: a hard MCR $A \rightarrow B \rightarrow C$

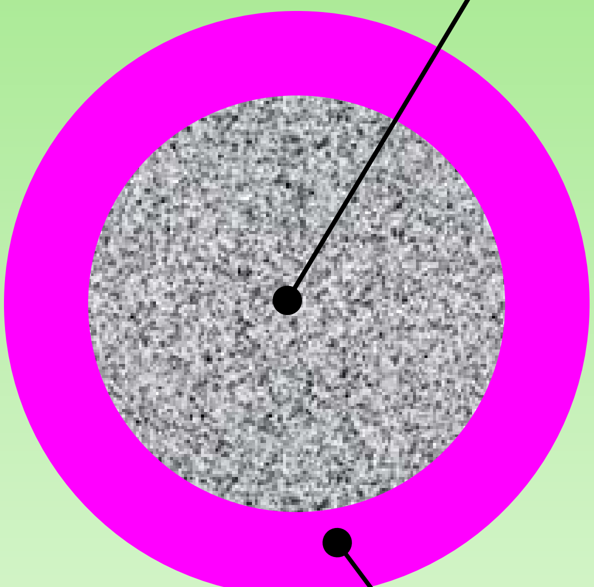


Example: a hard MCR $A \rightarrow B \rightarrow C$



Case study: Pellets' release

Sugar +API



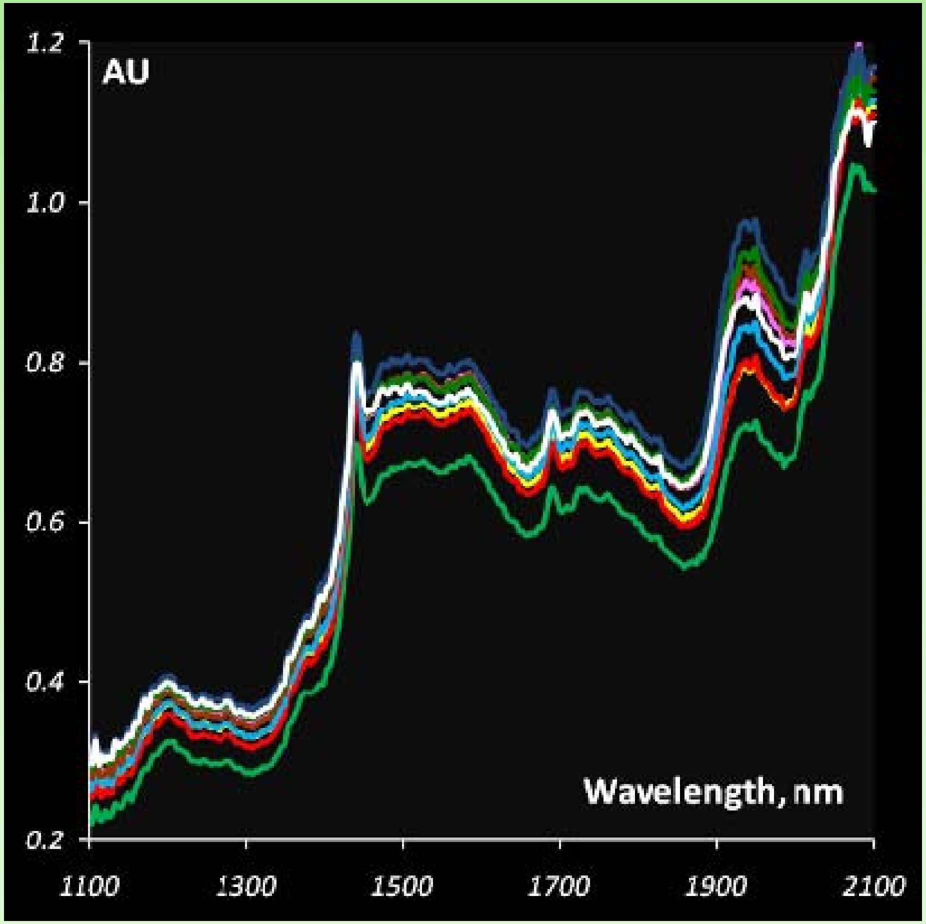
Coating: Acryl EZE

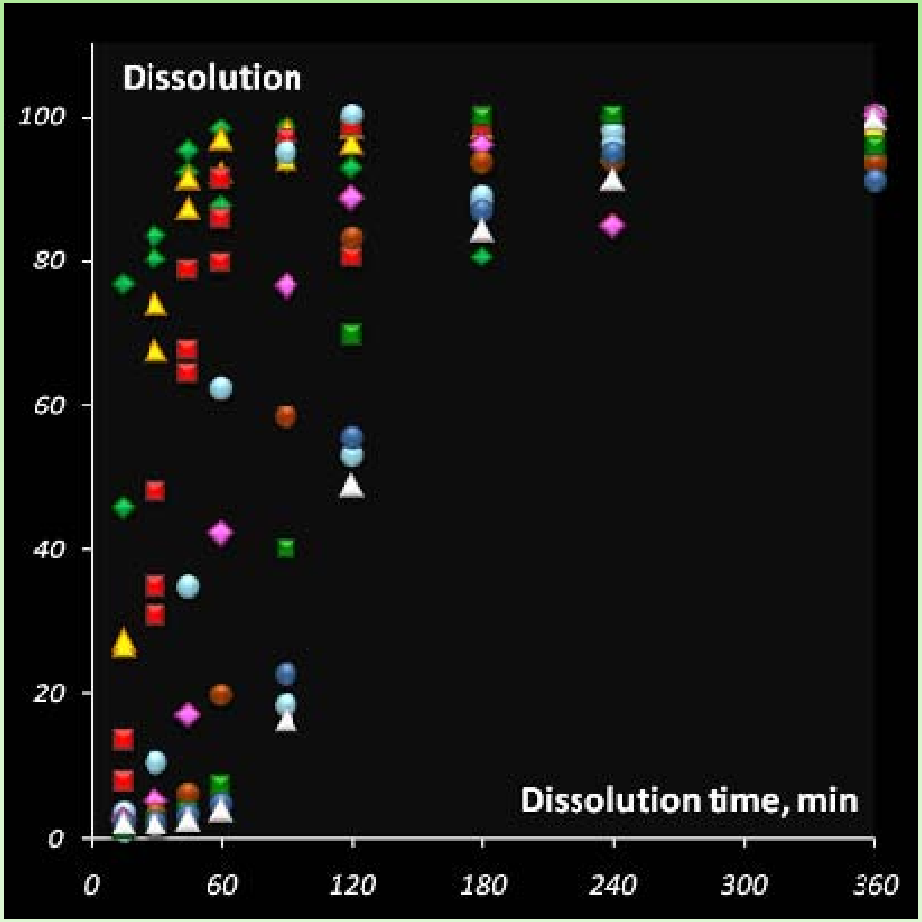
Experiment

NIR Spectra

Dissolution Profiles

***t* = 105**





Dissolution data

White dyer

Batch W1

Batch W2

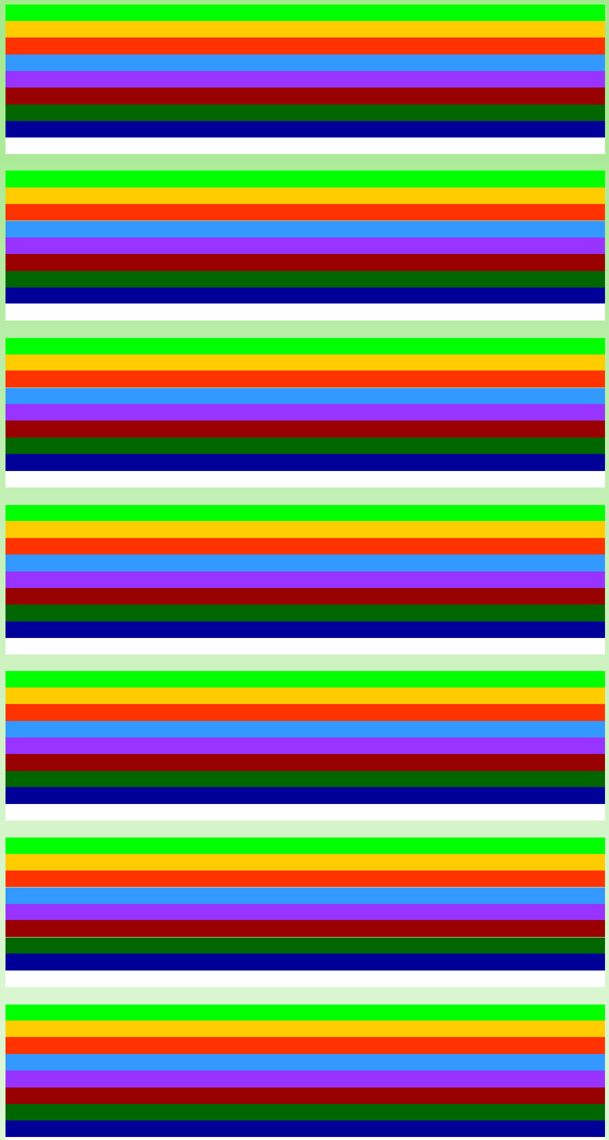
Batch W3

Batch W4

Batch W5

Batch W6

Batch W7



Yellow dyer

Batch Y1

Batch Y2

Batch Y3

Batch Y4

Batch Y5

Batch Y6

Autocatalysis

$$\varphi(t,m,k) = 100k\,\frac{\exp\left[(m+k)t\right]-1}{m+k\exp\left[(m+k)t\right]}$$

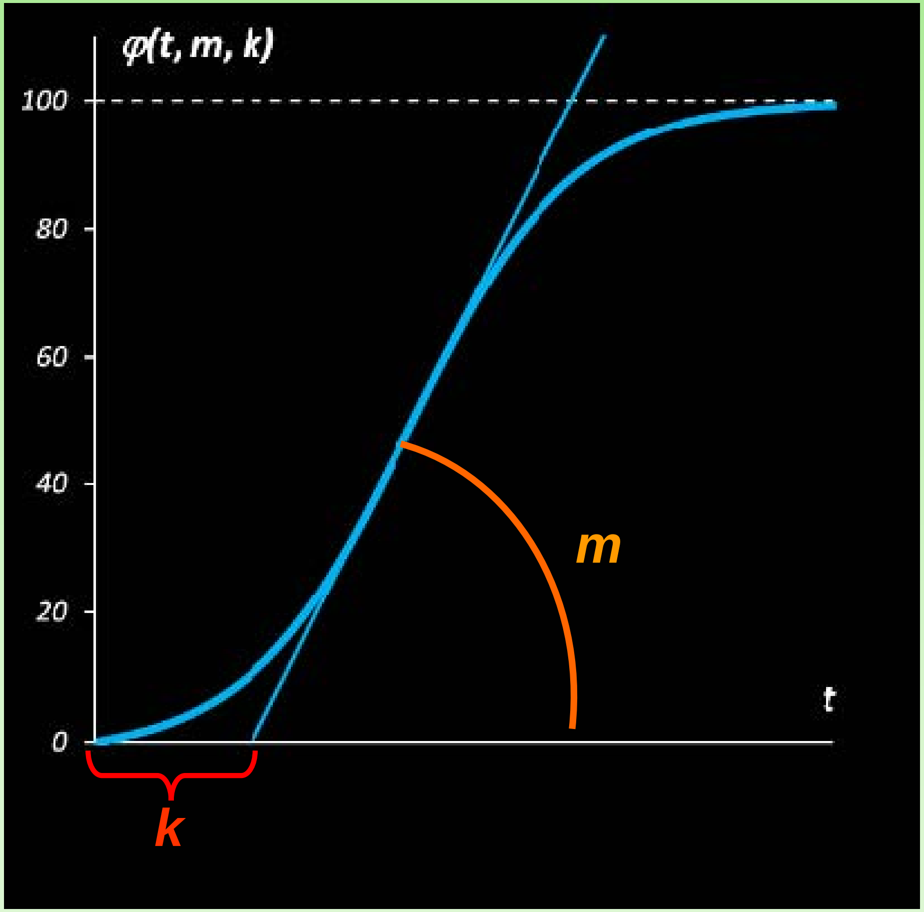
$$\mathrm{A} + \mathrm{B} \xrightarrow{m} 2\mathrm{B}$$

$$\mathrm{A} \xrightarrow{k} \mathrm{B}$$

$$[\mathrm{A}] + [\mathrm{B}] = 100$$

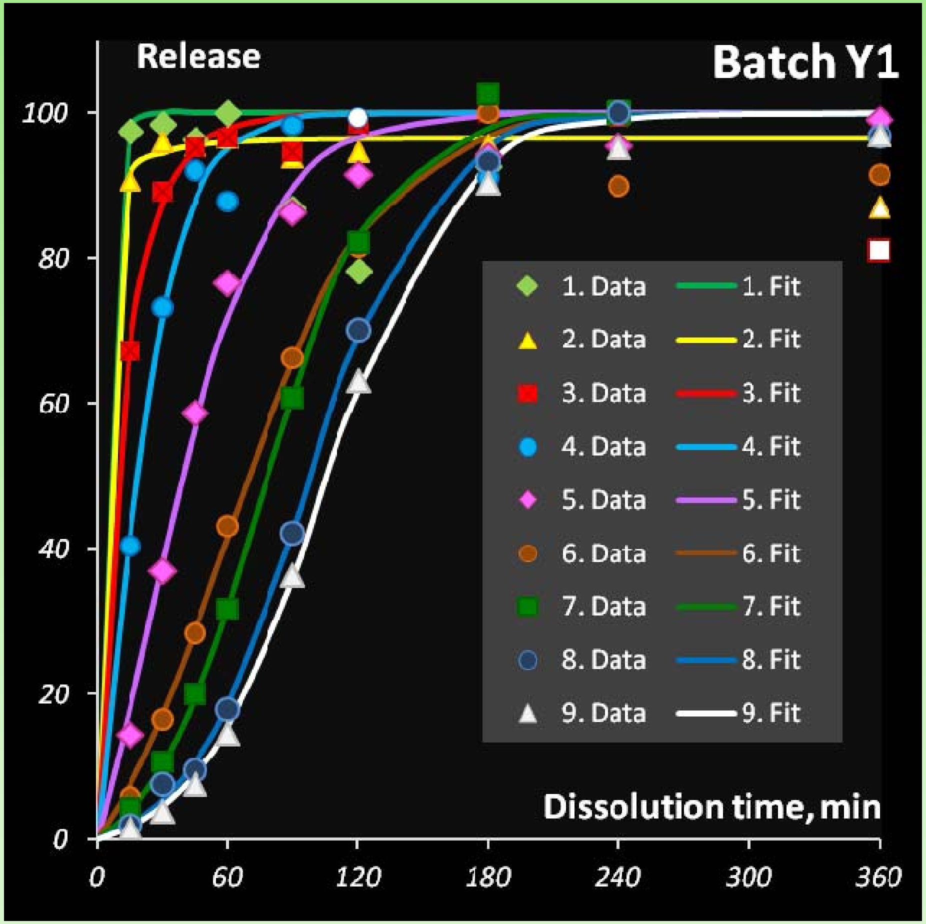
$$[\mathrm{B}](0) = 0$$

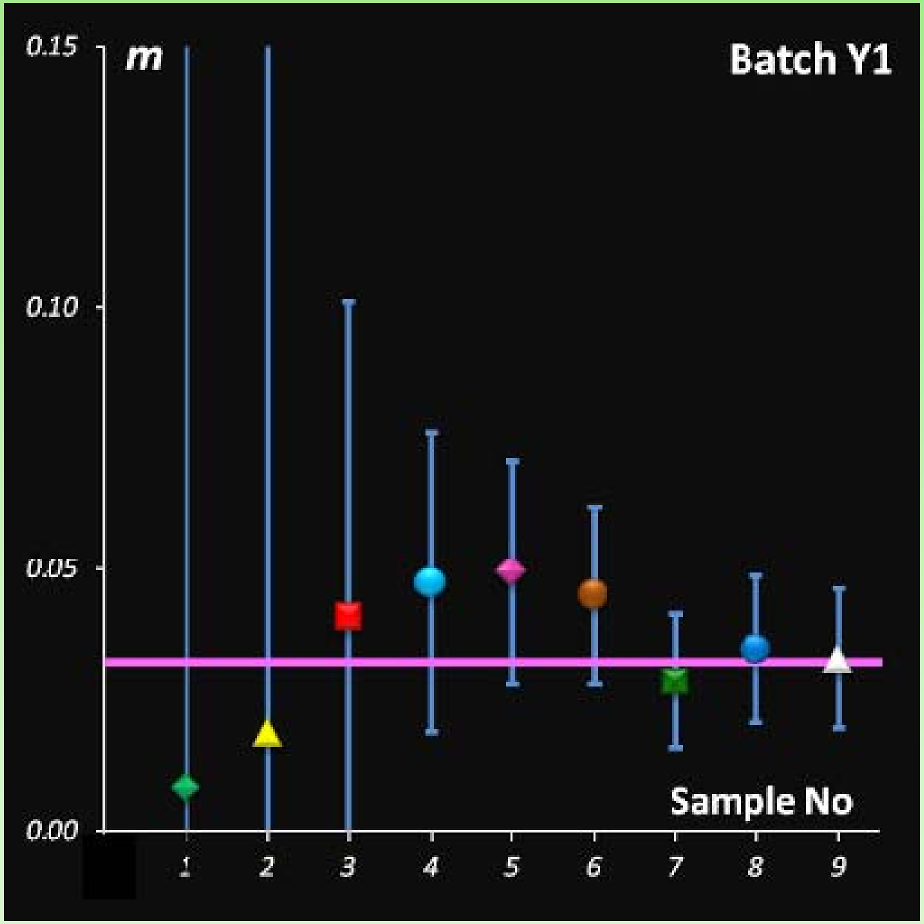
$$\varphi = [\mathrm{B}]$$



(7+6)*9 *k*'s + (7+6)*9 *m*'s = 234 unknown parameters

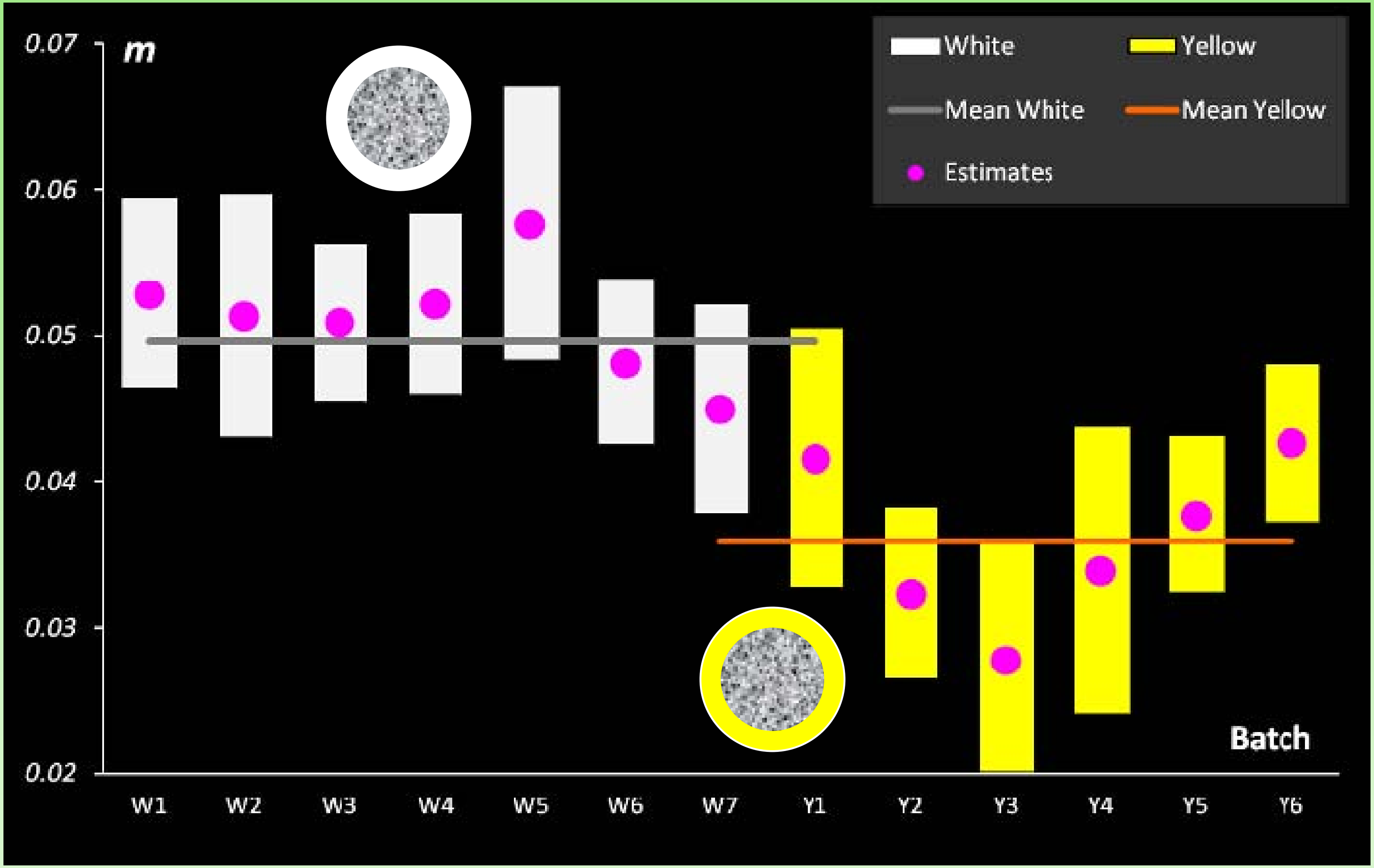
Parameter *m* is common within a batch





(7+6)*9 *k*'s + (7+6) *m*'s = 130 unknown parameters

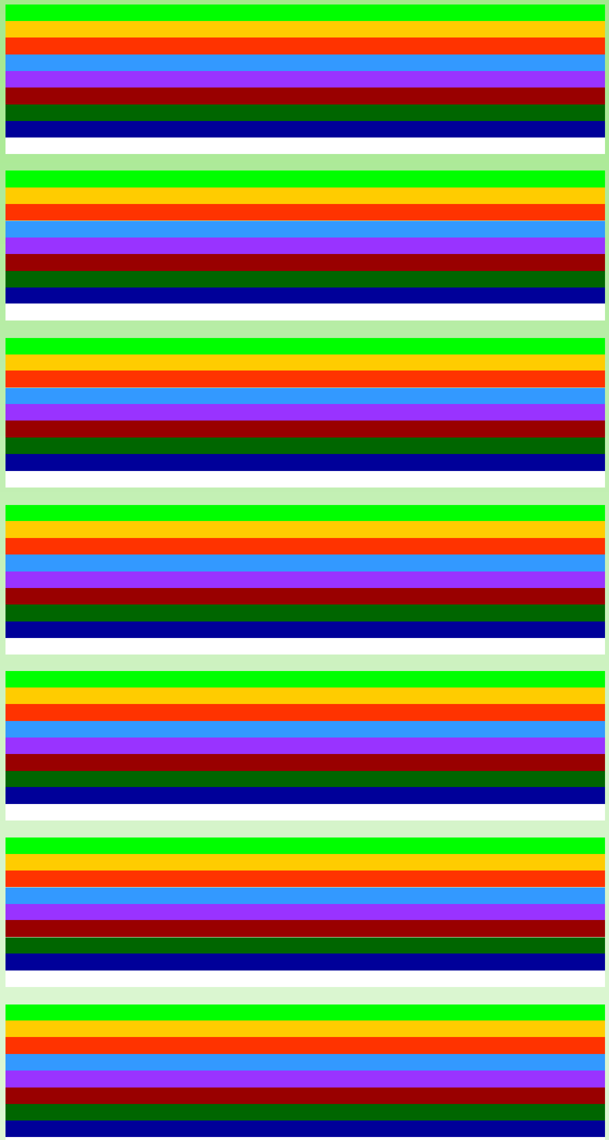
Parameter *m* and the layer grade



(7+6)*9 *k*'s + (1+1) *m*'s = 119 unknown parameters

White dyer batches

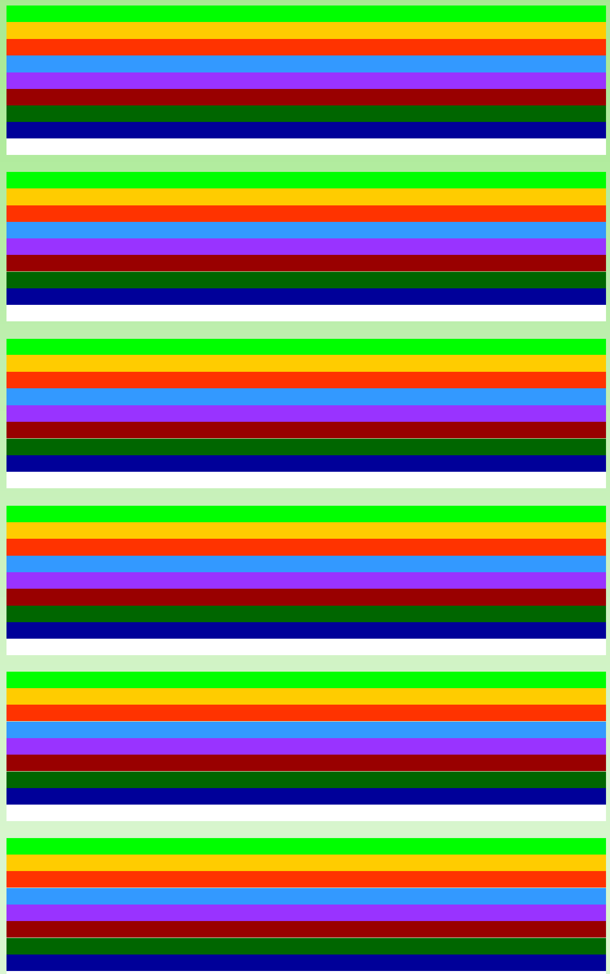
$$\varphi(t, m, k) = 100k \frac{\exp[(m+k)t] - 1}{m + k\exp[(m+k)t]}$$



Batch W1	$k_{11}, k_{12},\ldots, k_{19};$	m
Batch W2	$k_{21}, k_{22},\ldots, k_{29};$	m
Batch W3	$k_{31}, k_{32},\ldots, k_{39};$	m
Batch W4	$k_{41}, k_{42},\ldots, k_{49};$	m
Batch W5	$k_{51}, k_{52},\ldots, k_{59};$	m
Batch W6	$k_{61}, k_{62},\ldots, k_{69};$	m
Batch W7	$k_{71}, k_{72},\ldots, k_{79};$	m

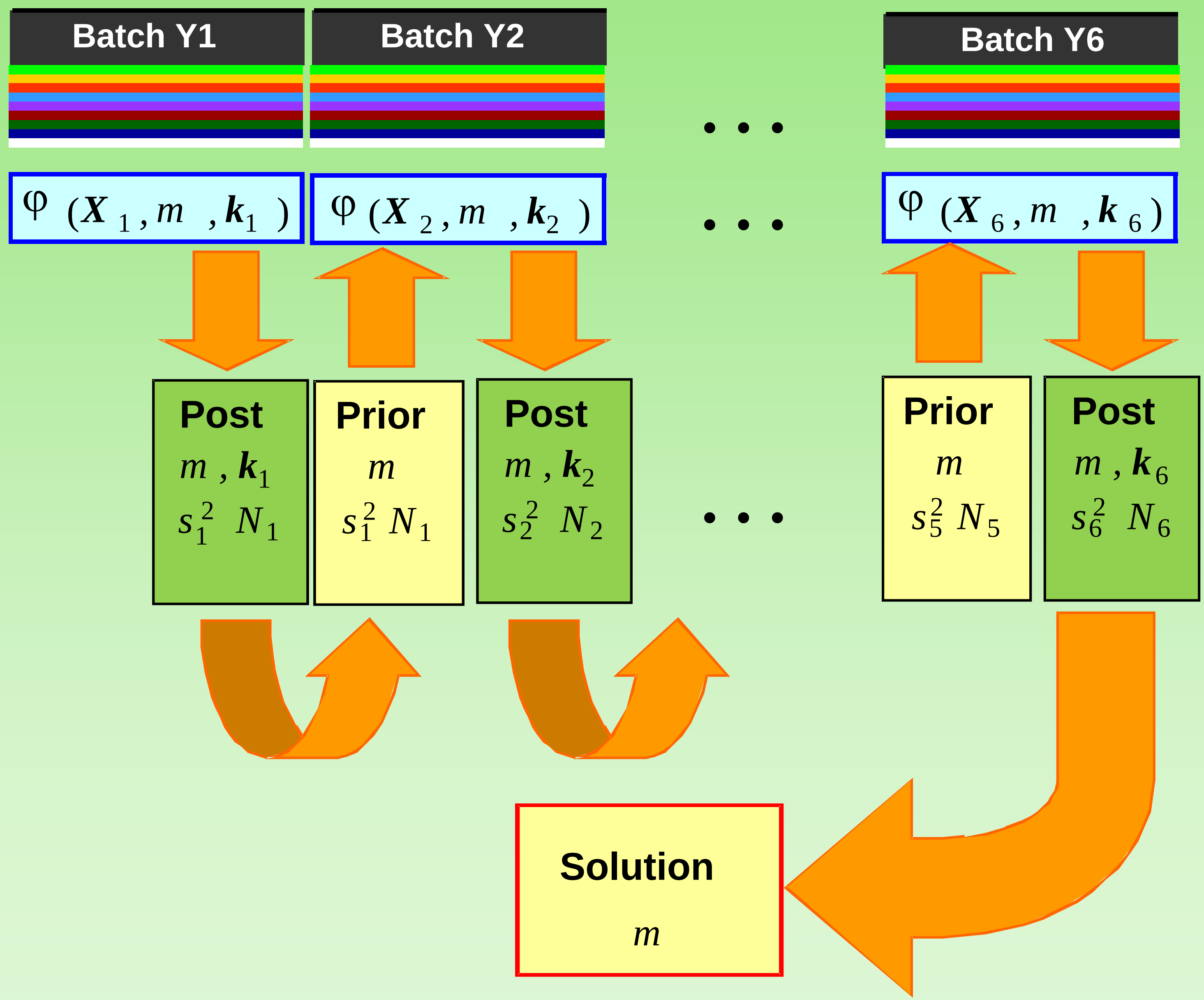
Yellow dyer batches

$$\varphi(t,m,k) = 100k\,\frac{\exp\left[(m+k)t\right]-1}{m+k\exp\left[(m+k)t\right]}$$

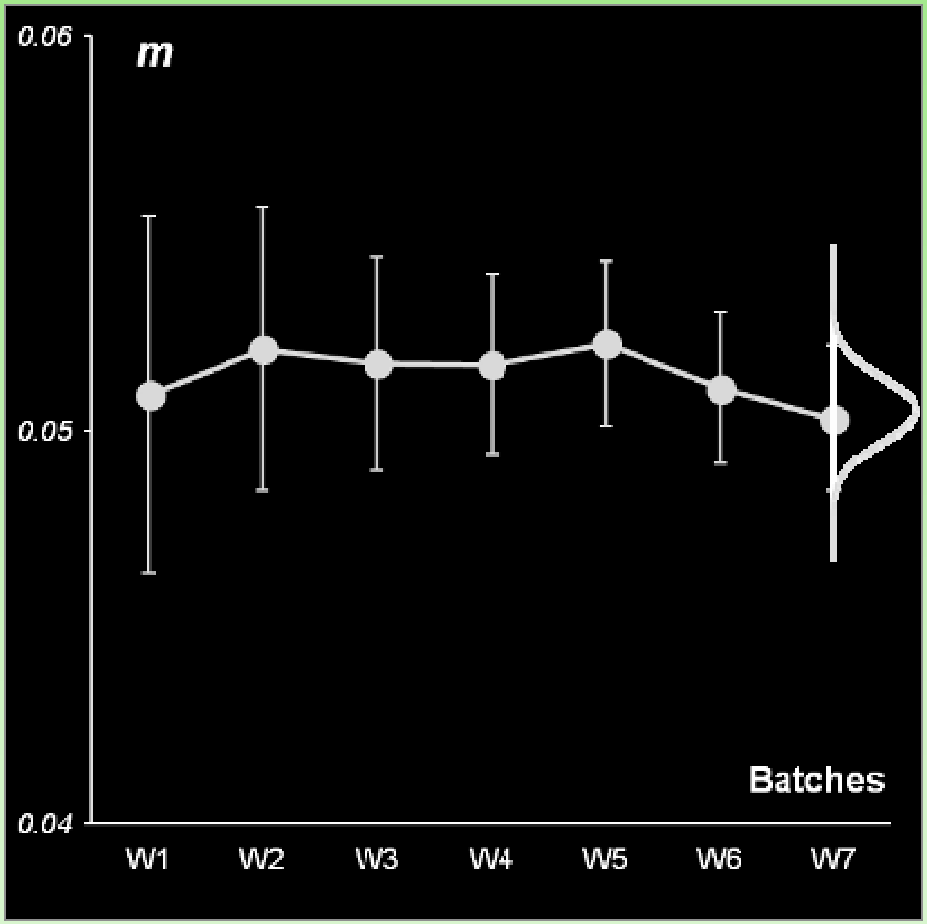


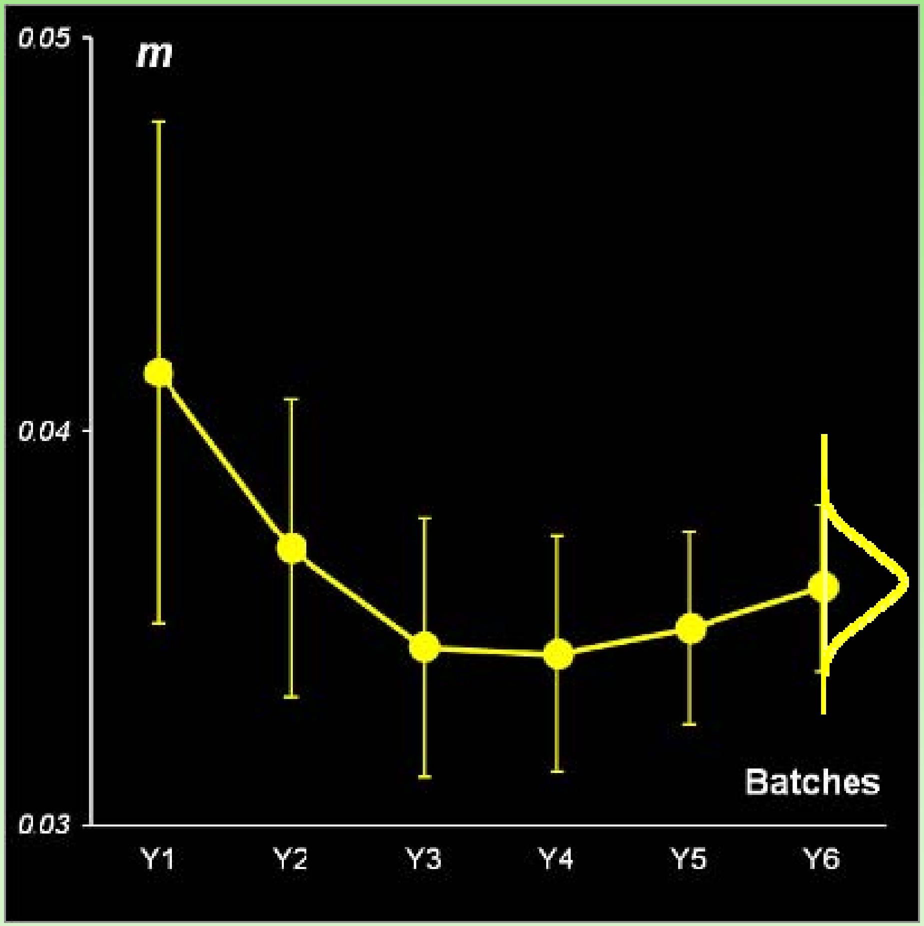
Batch Y1	$k_{11}, k_{12},\ldots, k_{19};$	m
Batch Y2	$k_{21}, k_{22},\ldots, k_{29};$	m
Batch Y3	$k_{31}, k_{32},\ldots, k_{39};$	m
Batch Y4	$k_{41}, k_{42},\ldots, k_{49};$	m
Batch Y5	$k_{51}, k_{52},\ldots, k_{59};$	m
Batch Y6	$k_{61}, k_{62},\ldots, k_{69};$	m

Forward SBE procedure

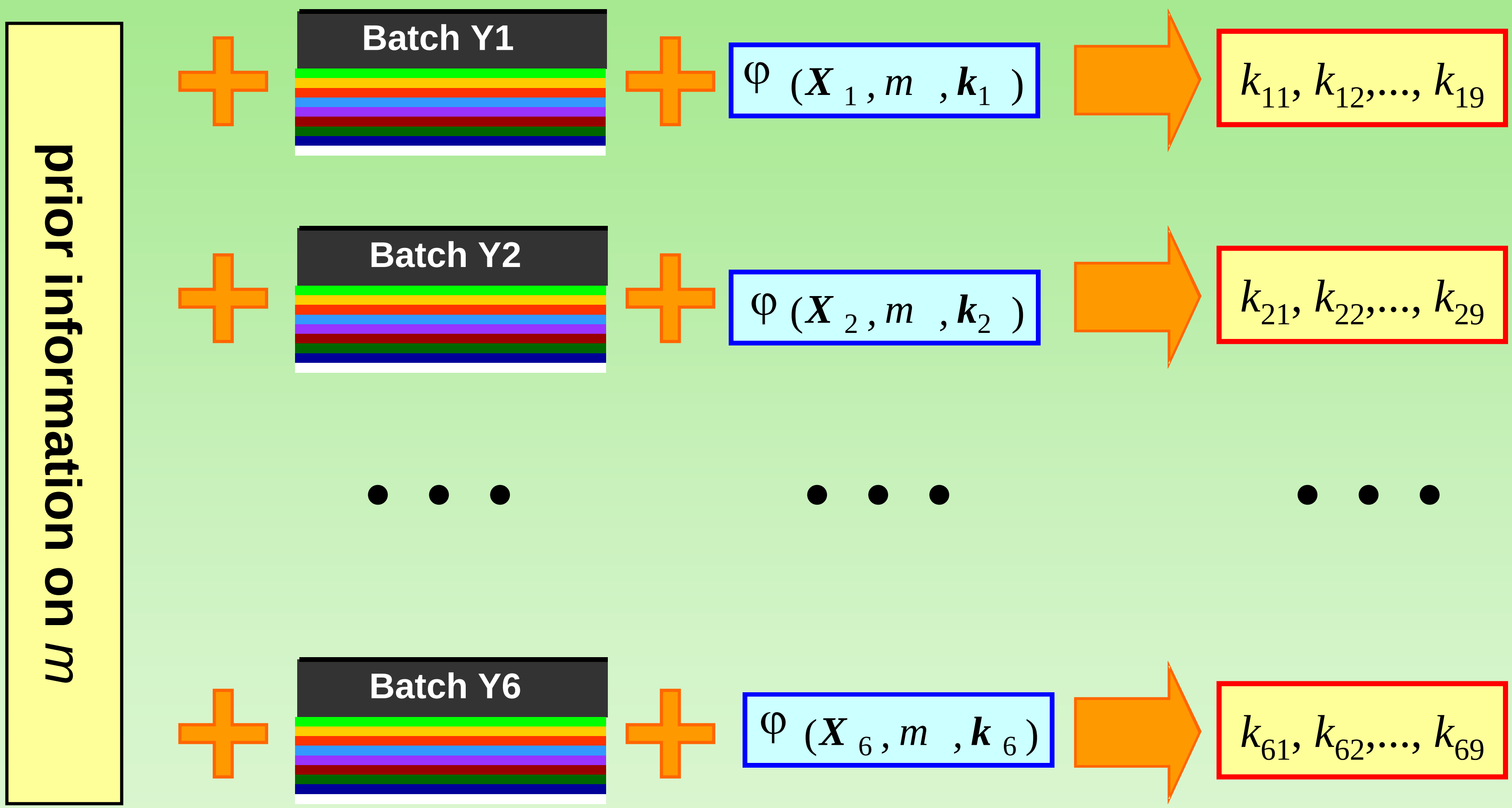


Successive estimates of *m*

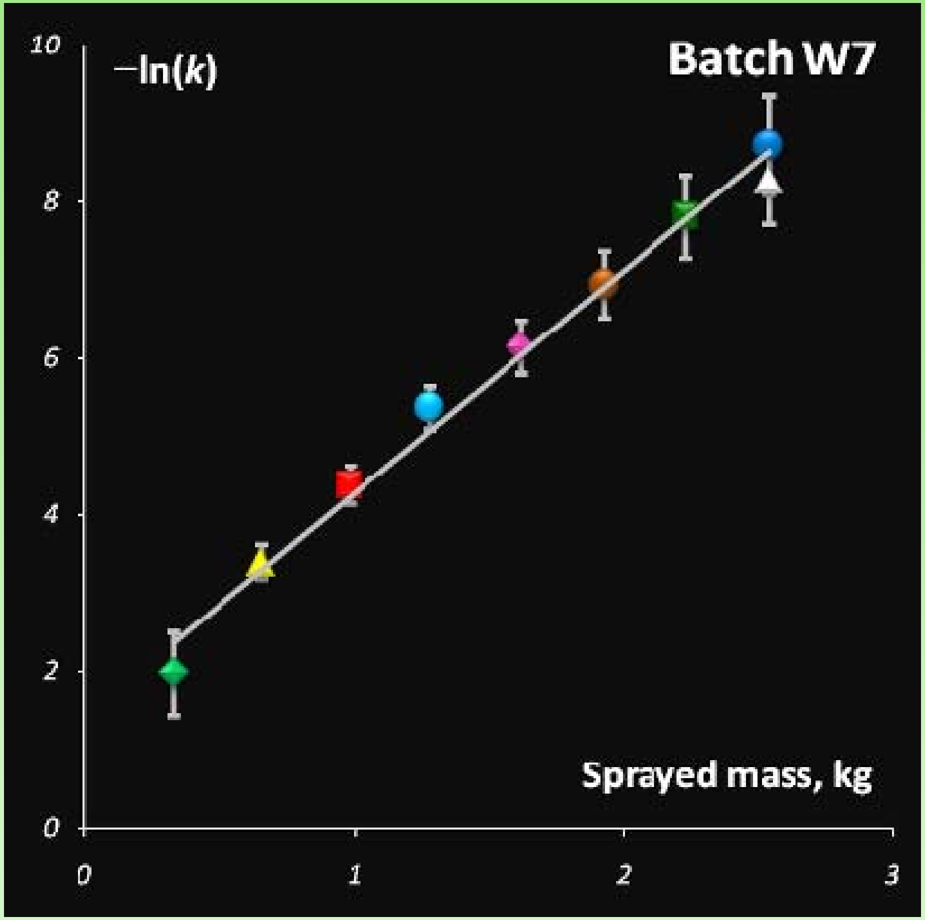


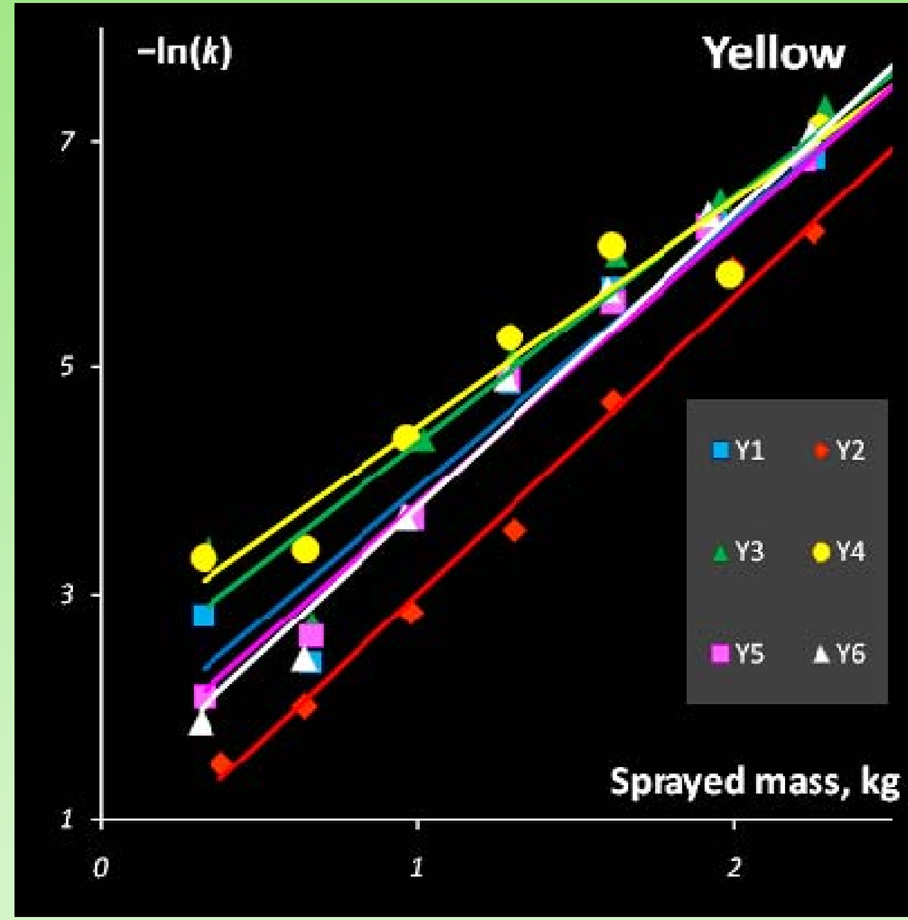


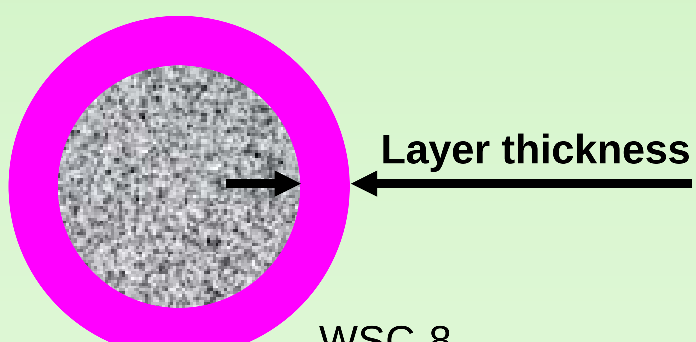
Backward SBE procedure



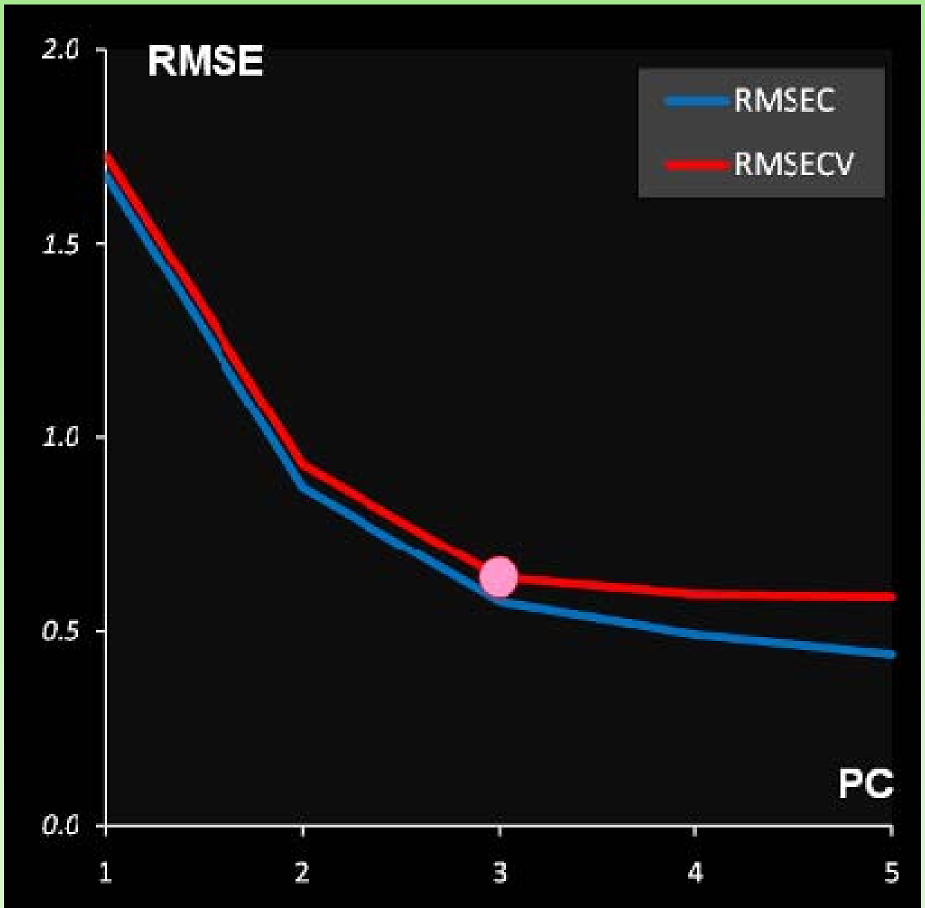
Parameter *k* and the layer thickness

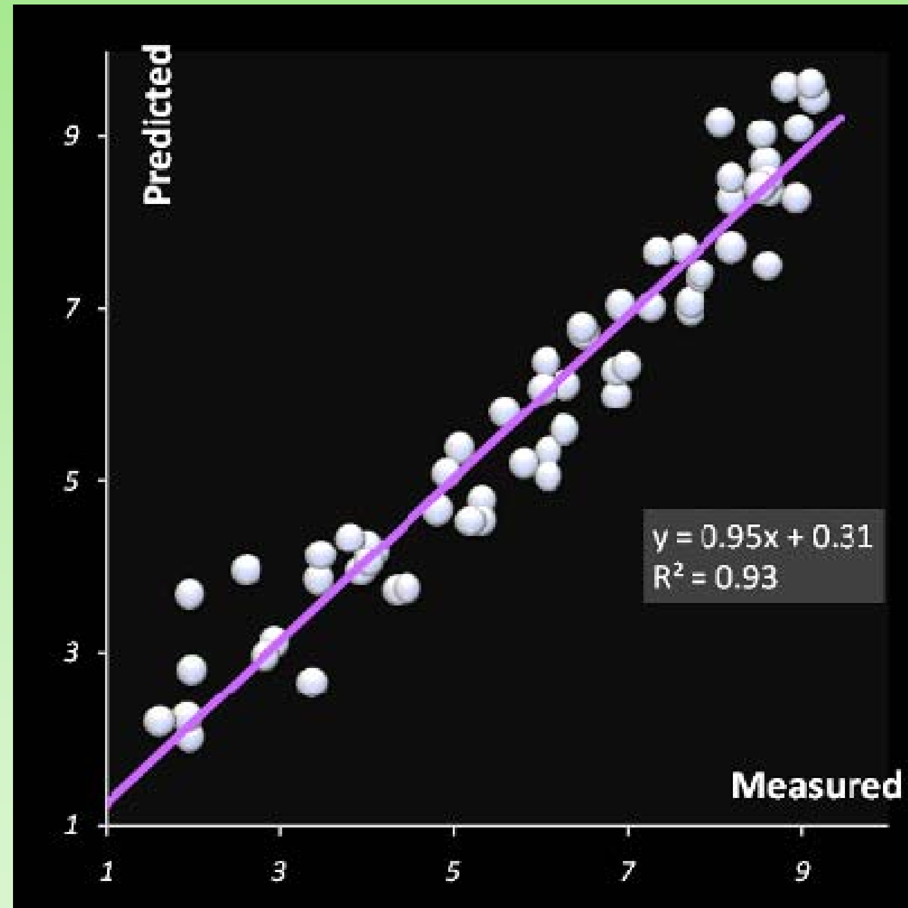




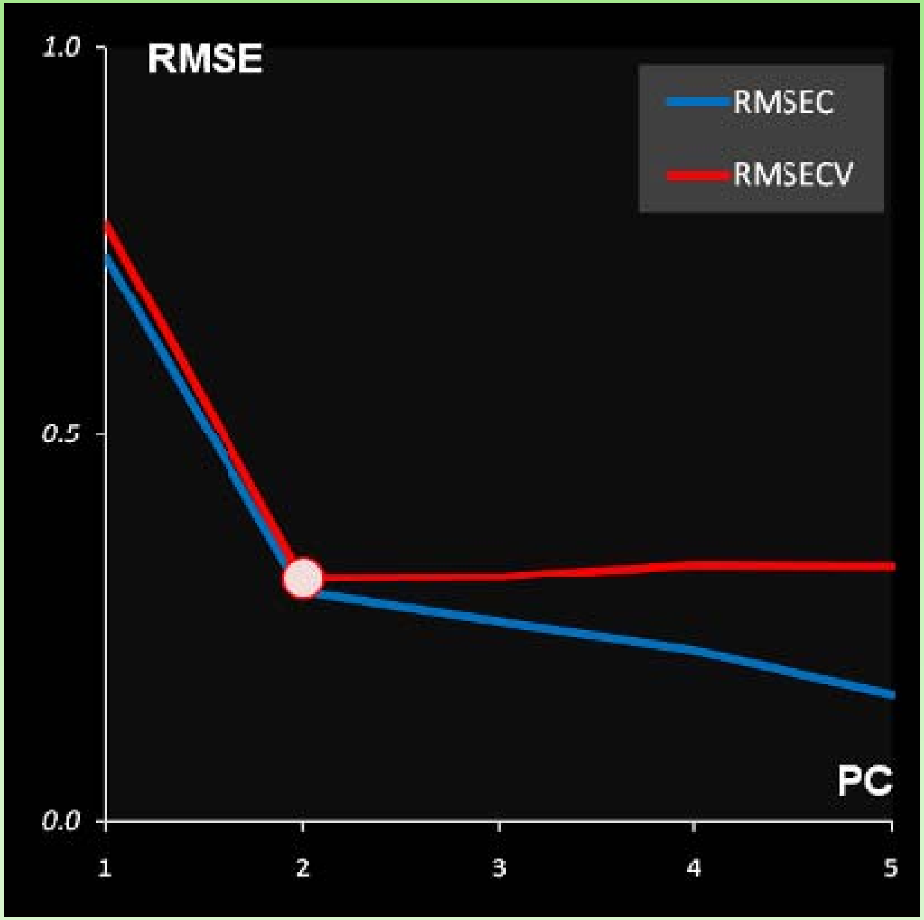


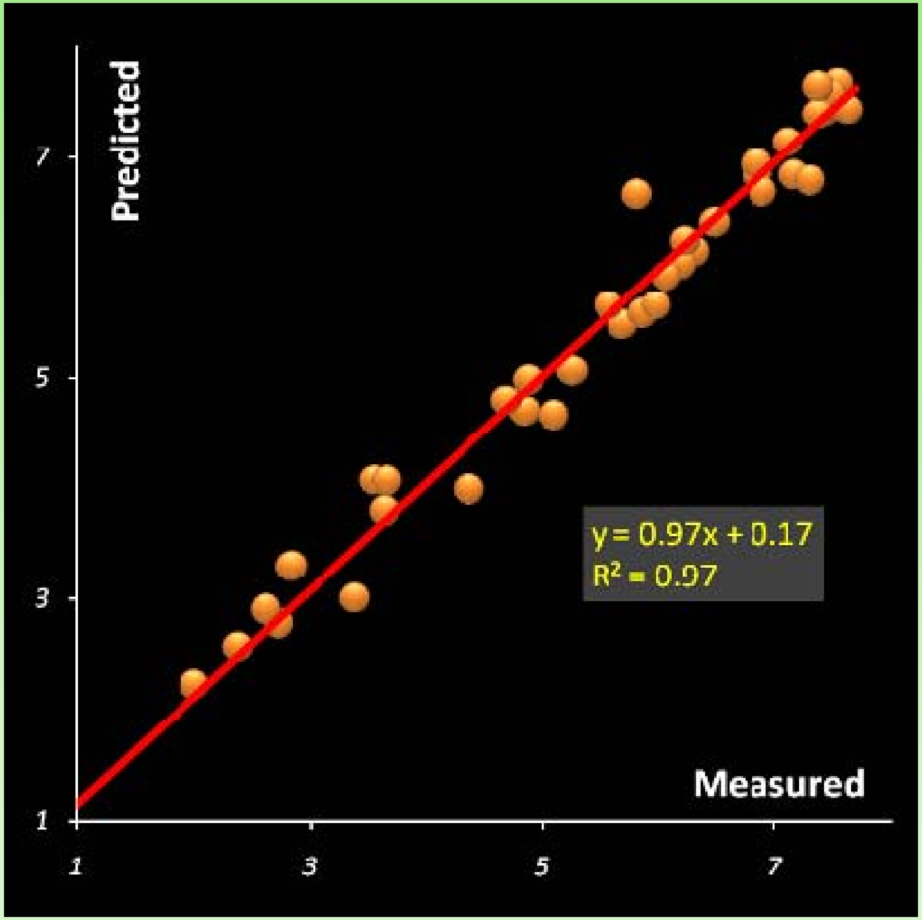
NIR prediction of *k*: White subset





NIR prediction of *k*: Yellow subset





Conclusions

White models: formal kinetics, mechanism, rate constants, etc

Semen Spivak

Grey models: curve resolution, pure components, etc

Cyril Ruckebusch & Veli-Matti Taavitsainen

Black models: features extraction, ‘pre-processing’ for MVA

me