Chemical water detection – Oven coulometric Karl Fischer titration (O-cKF)

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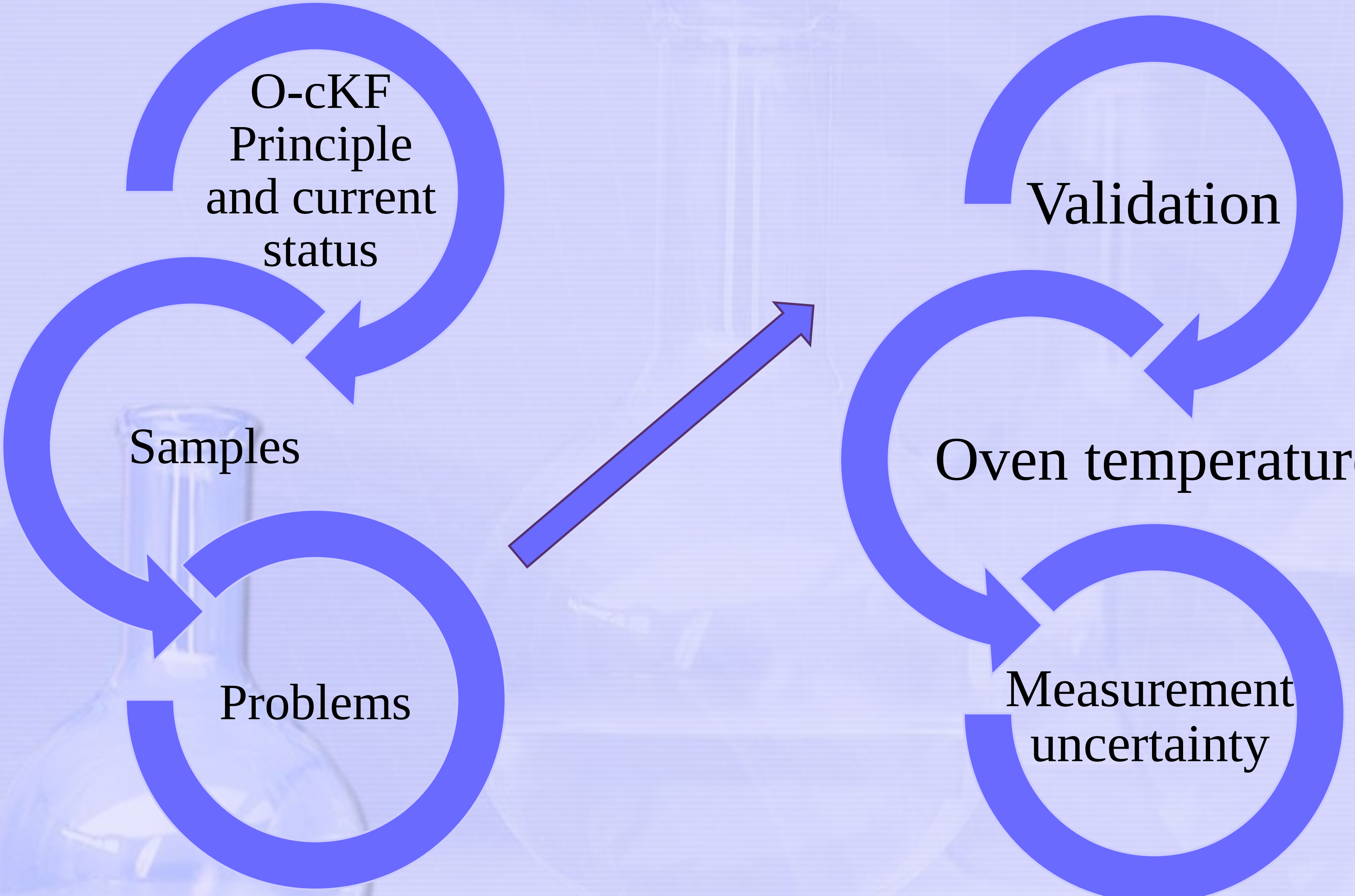

O-cKF Principle and current status
Samples
Problems
Validation
Oven temperature
Measurement uncertainty

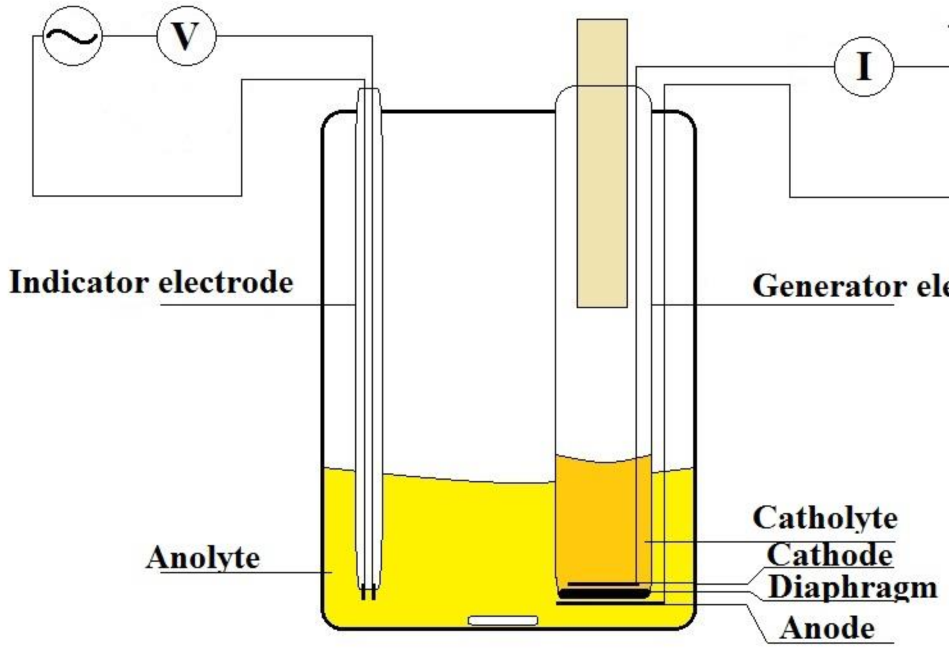
cKF: Principle

First step:

$$ROH + SO_2 + R'N \longrightarrow [R'NH]SO_3R \qquad (1)$$

Second step:

$$[R'NH]SO_3R + H_2O + I_2 + 2R'N \longrightarrow 2[R'NH]I + [R'NH]SO_4R \qquad (2)$$



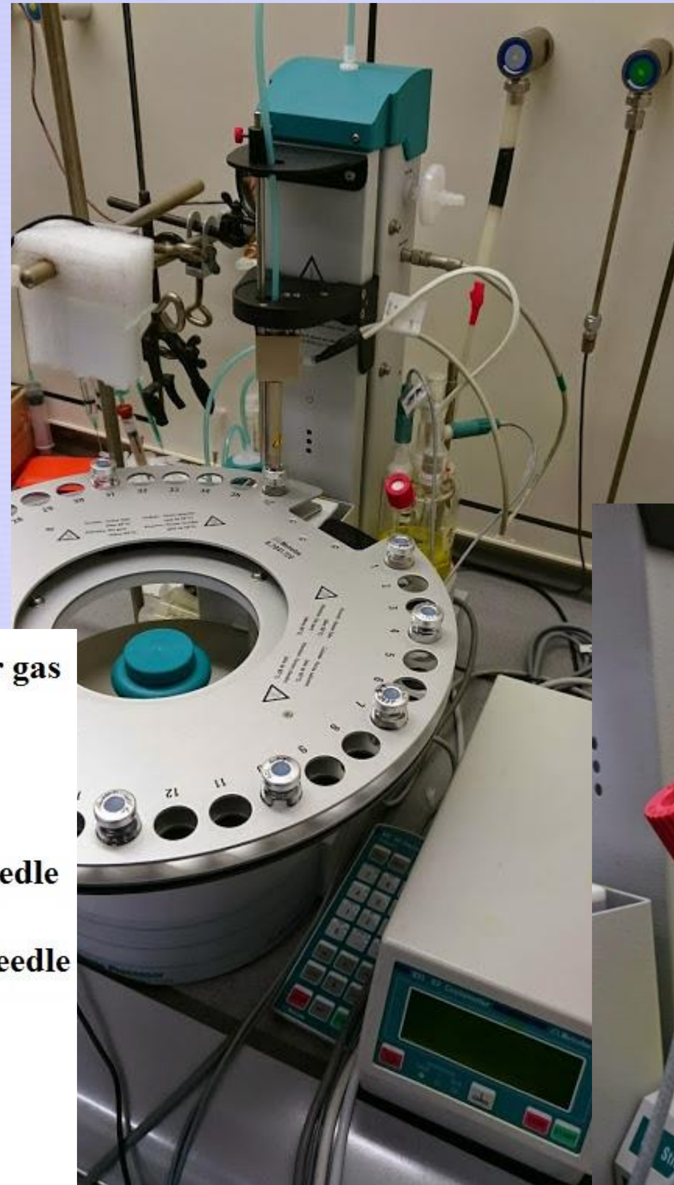
Anode reaction:

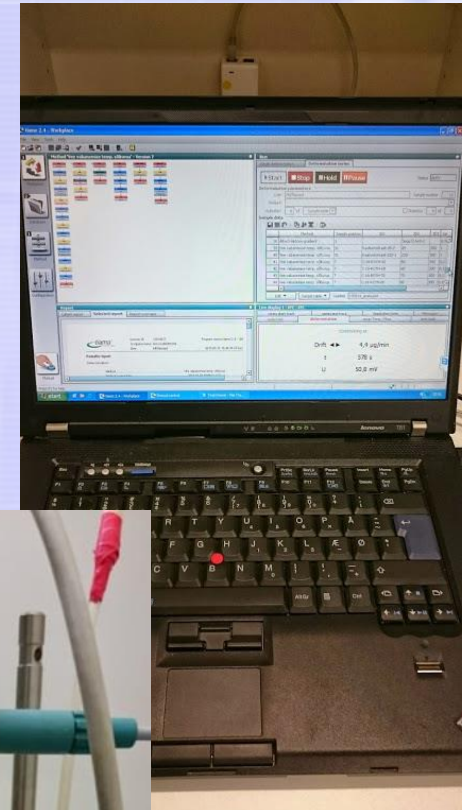
$$2\,I^- - 2\,e^- \longrightarrow I_2 \qquad (3)$$

Cathode reaction:

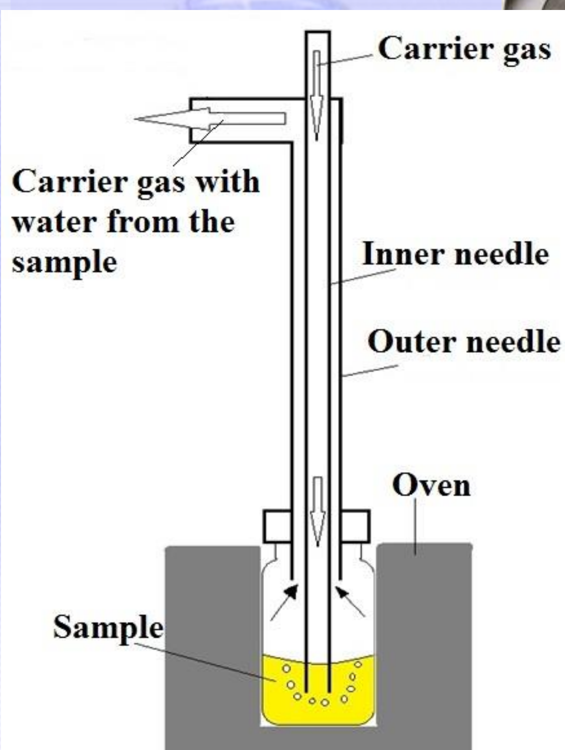
$$2\,H^+ + 2\,e^- \longrightarrow H_2\uparrow \qquad (4)$$

O-cKF






Metrohm


Carrier gas
Carrier gas with water from the sample
Inner needle
Outer needle
Oven
Sample

cKF: Status

In Liquids

- **Well established, well understood**
- **Generally considered the standard method**
- **Low uncertainties**

In Solids

- **Extensively used, but poorly understood**
  - **Different types of water**
  - **Sample inhomogeneity**
  - **Strong matrix effects**
- **Often considered standard method, but work is still needed**
- **Uncertainty estimates generally not reliable**

Thus the need for: METefnet

Problems

- Many samples are too complex to obtain a reliable measured value
  - water content instability
  - different forms of water
  - sample inhomogeneity
  - partial decomposition with release of water
- Measured values are not uniformly defined – results are incomparable
- Measurement systems work on different principles, resulting in large differences of measured values
- How to calculate measurement uncertainty?

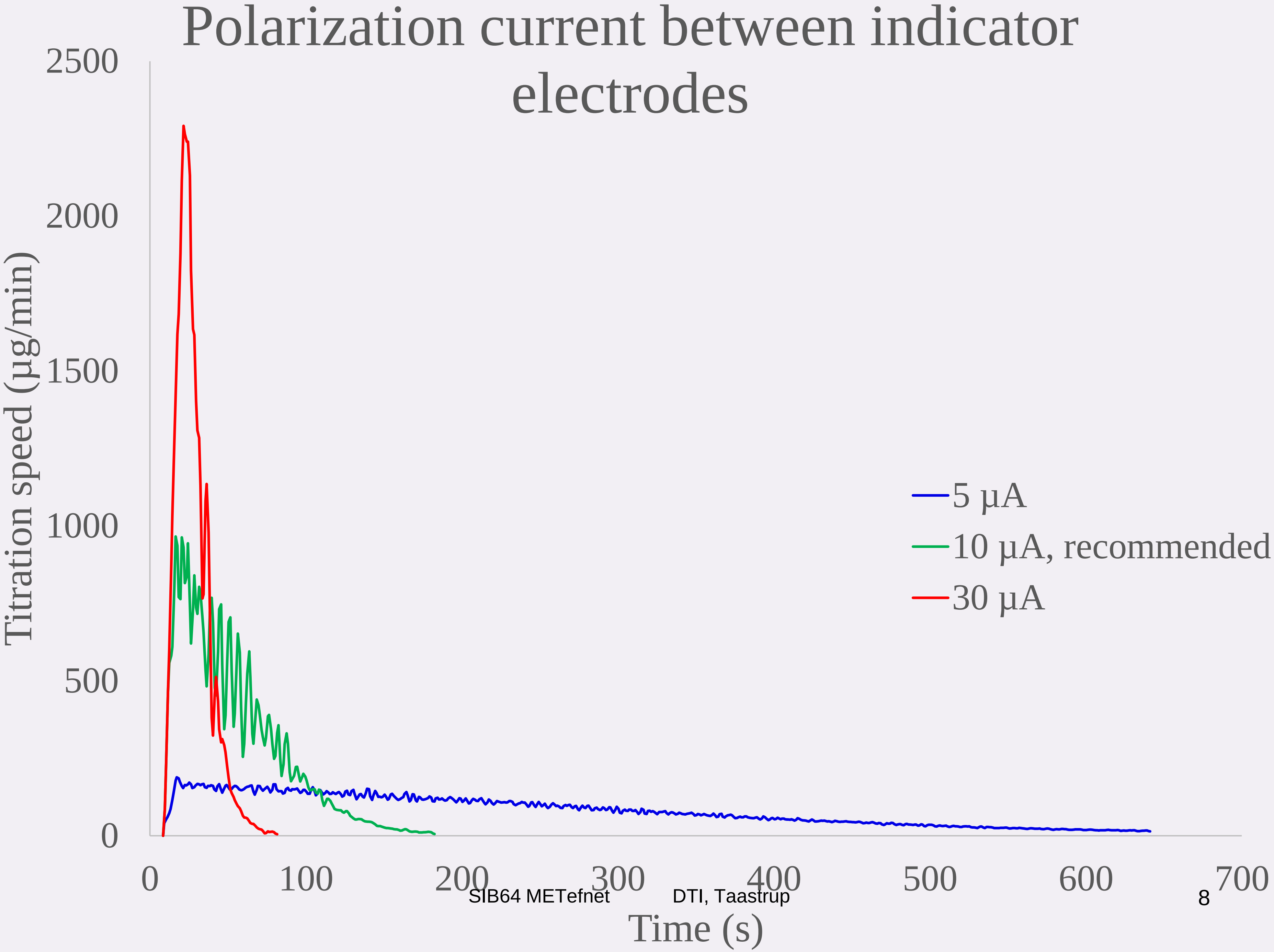
Validation

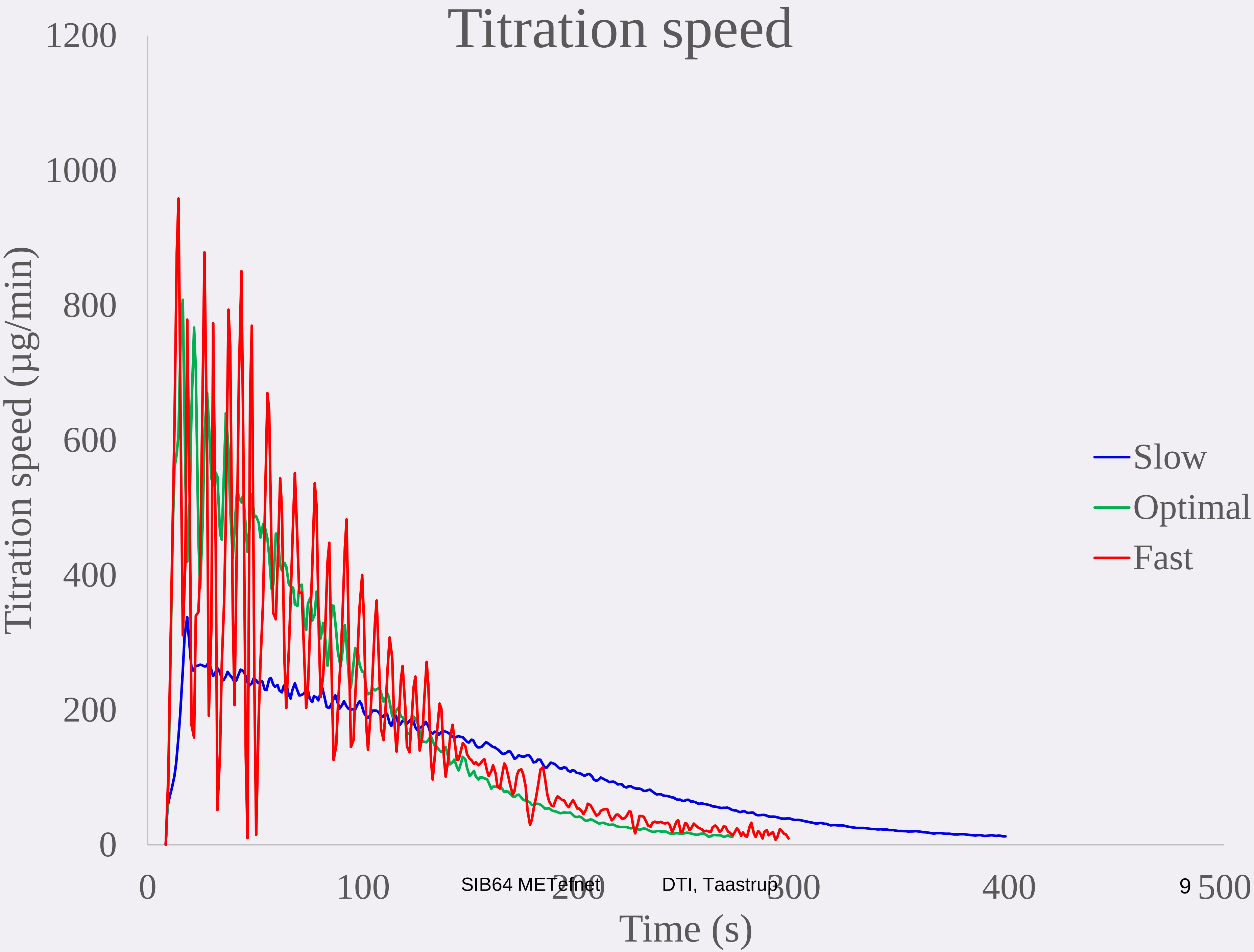
Coulometric titrator parameters

- **Polarization current between indicator electrodes**
- Threshold potential between the indicator electrodes
- Time interval between measurement points
- **Titration speed**
- End-point criterion
  - Relative drift
  - Absolute drift

Oven system parameters

- **Oven temperature**
- Carrier gas and its flow rate

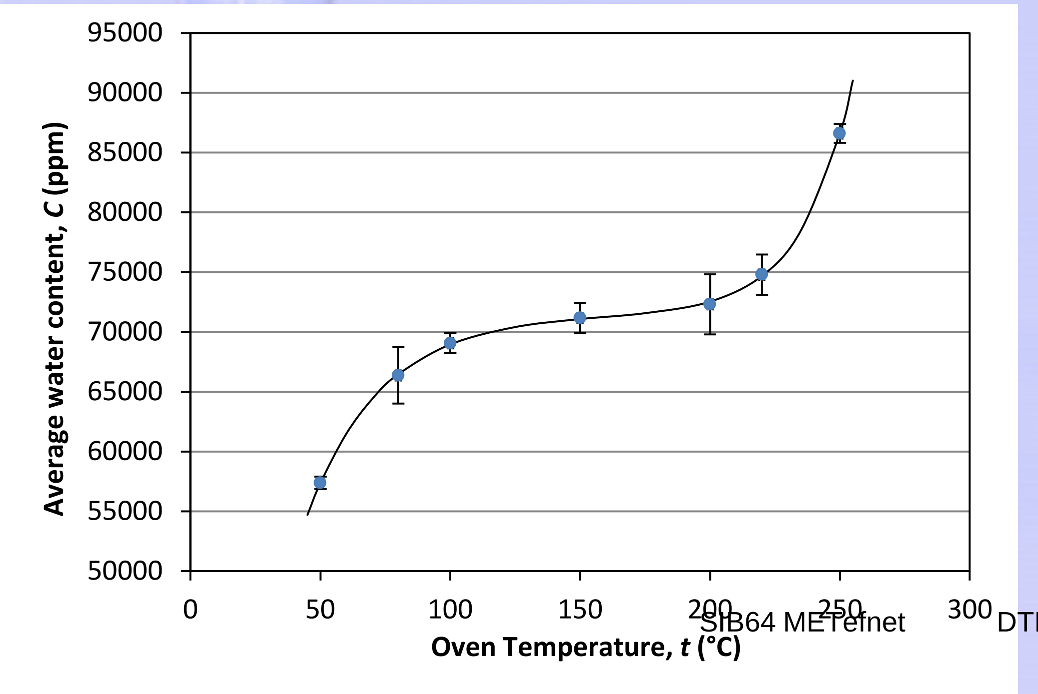

Polarization current between indicator electrodes
Titration speed (µg/min)
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
700
Time (s)
5 µA
10 µA, recommended
30 µA


Titration speed
1200
1000
800
600
400
200
0
Titration speed (µg/min)
0
100
200
300
400
500
Time (s)
Slow
Optimal
Fast

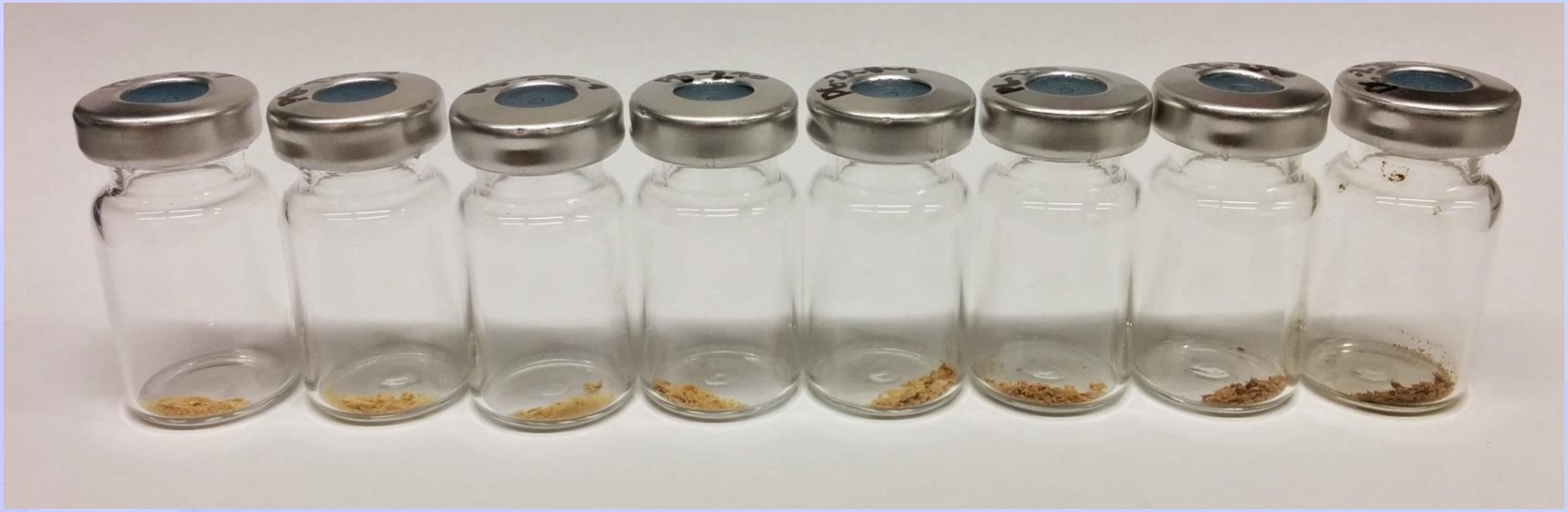
Dependence of wood water content measurement result on oven temperature

Oven temperature

- **LoD** uses **long** heating times: **temperatures slightly above 100 °C are OK**
- **cKF** uses **short** heating times: **temperatures slightly above 100 °C are not OK**
  - Using long heating times in cKF is not practical



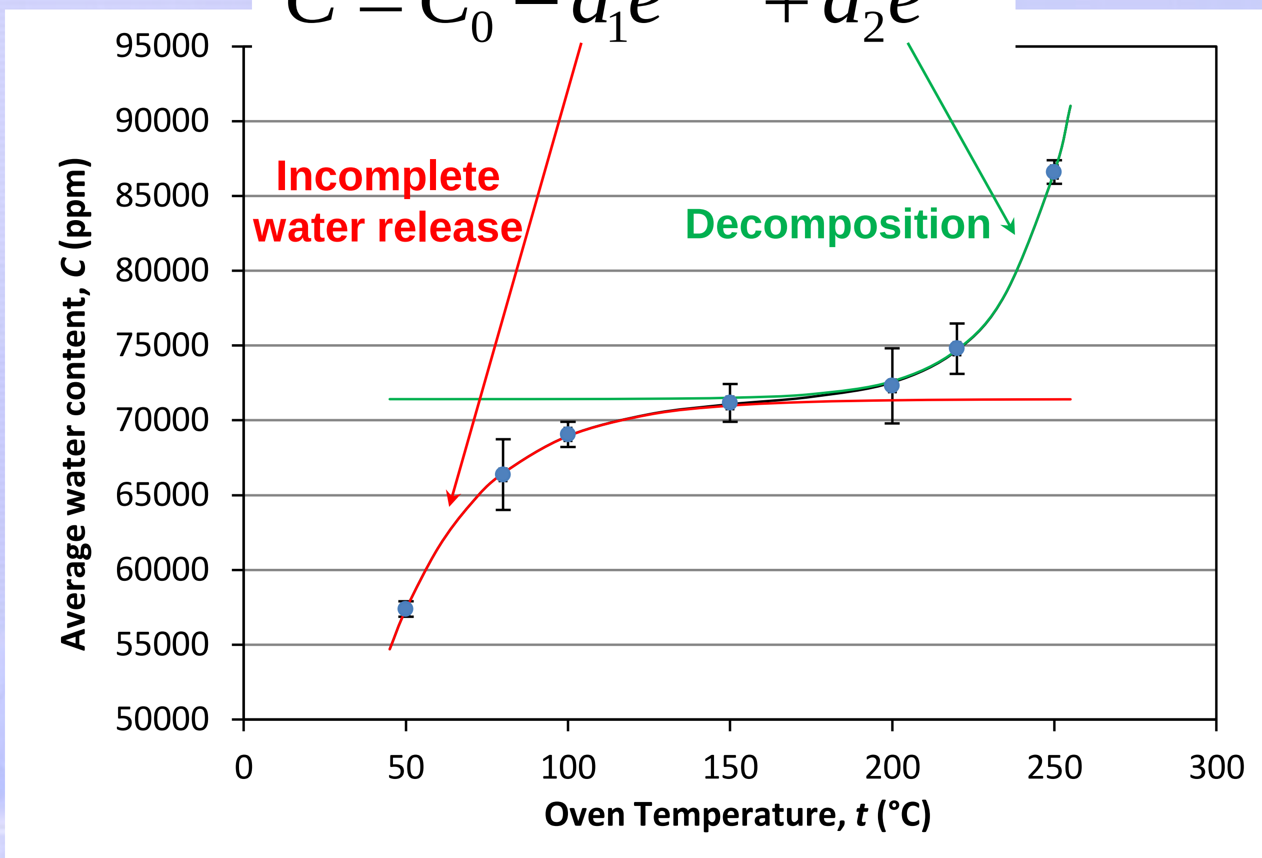
Effect of heating temperature on wood



After heating: 50°C 150°C 200°C 210°C 220°C 230°C 240°C 250°C.

Dependence of wood water content measurement result on oven temperature: the processes

$$C = C_0 - a_1 e^{-b_1 t} + a_2 e^{b_2 t}$$

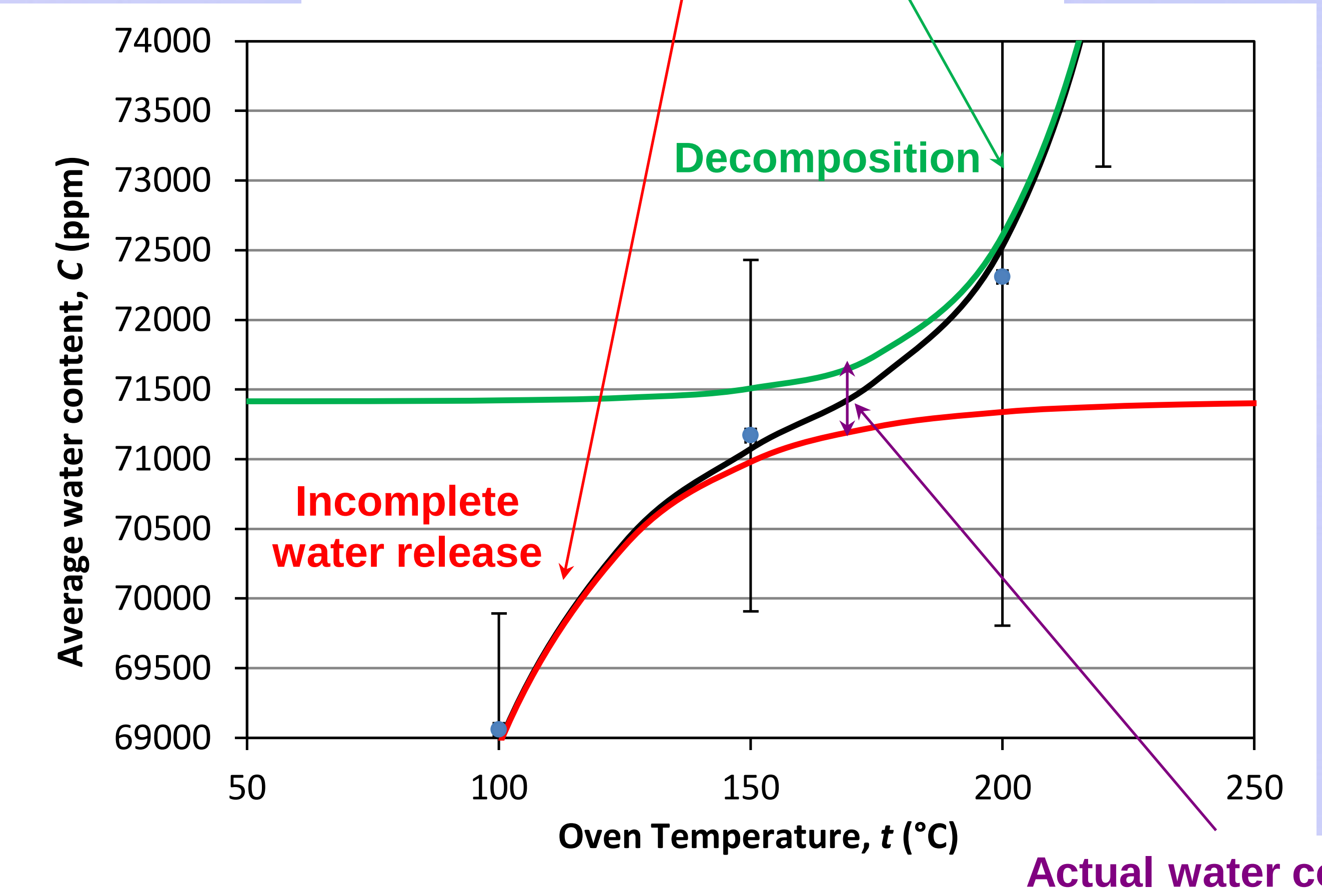


Least squares fitting:

Parameter	Value
Plateau, C0:	71415
Lower offset, a1:	79943
Lower shape, b1x1000:	34.77
Higher offset, 1/a2:	22.21
Higher shape, b2x1000:	50.92

Dependence of wood water content measurement result on oven temperature: the processes

$$C = C_0 - a_1 e^{-b_1 t} + a_2 e^{b_2 t}$$



Actual water content:
C_0 = 71415 ppm
(7.1 g/100g)

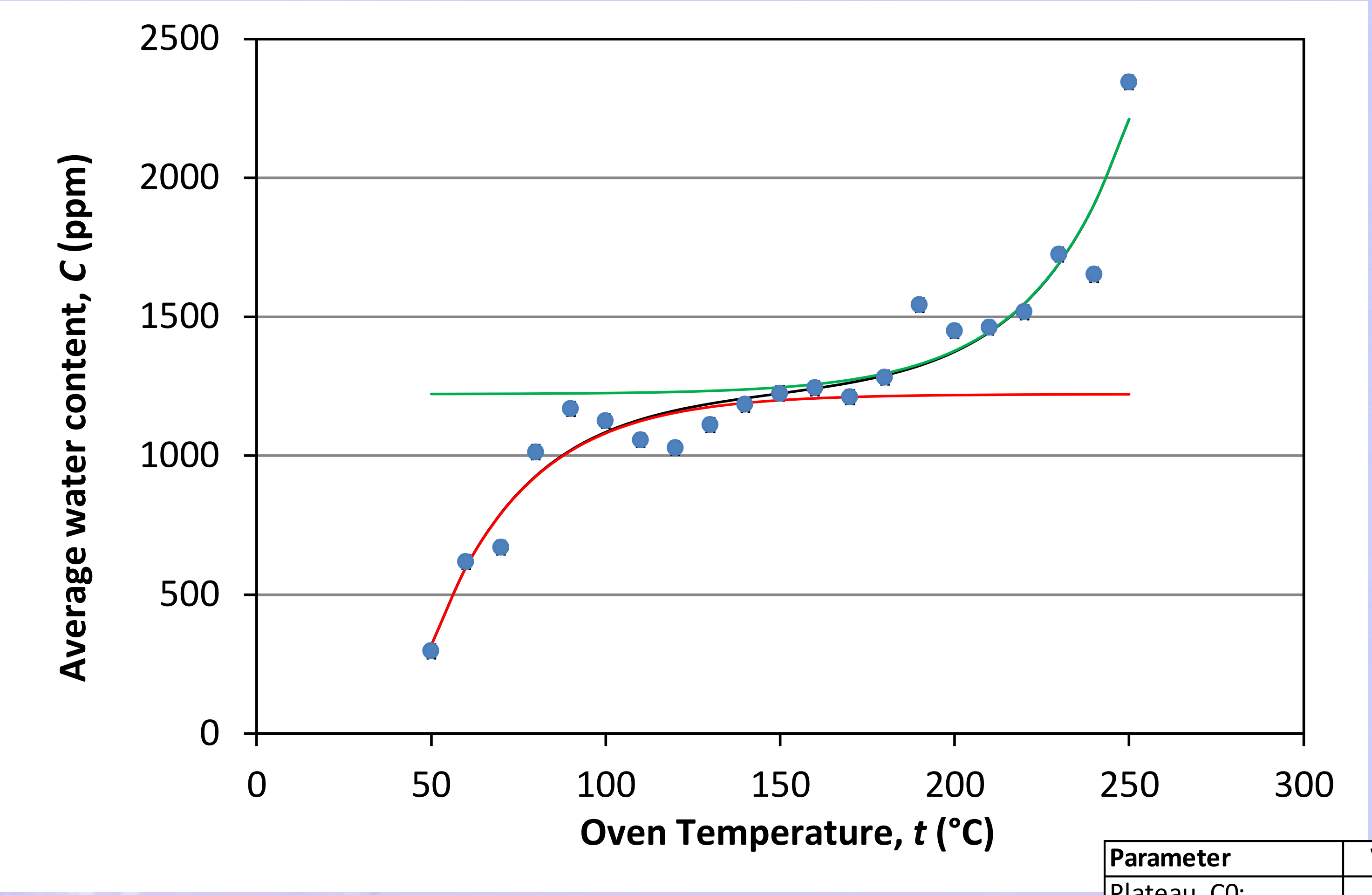
Samples

	Sample	H_2O g/100g
High water content	Keratin	1.9 – 2.1
	C-8 stationary phase, laboratory conditions	2.0 – 2.3
	PSA stationary phase, laboratory conditions	2.3 – 2.4
	C-8 stationary phase, hygrostate	4.1 – 4.7
	Paper, Logic 300	4.2 – 6.3
	Meat bone meal	2 – 5 %
	Alpha-D-lactose monohydrate, bottled	5.0
	Potassium citrate, dried at 70°C	5.6 – 5.7
	Potassium citrate, dried at 120°C	5.3 – 5.5
	Wood pellet, analyzed at 150°C	6.9 – 7.1
	Wood pellet, analyzed at 103°C	6.4 – 7.4
	PSA stationary phase, hygrostate	6.1 – 34
	Calcium oxalate monohydrate, bottled	12.3 – 12.4

	Sample	H_2O g/100g
Low water content	Parafilm M, laboratory conditions	0.001 – 0.03
	Candle wax, laboratory conditions	0.005 – 0.02
	Candle wax, hygrostate	0.01 – 0.04
	Parafilm M, hygrostate	0.04 – 0.2
	Polymorph (Polycaprolactone)	0.15 – 0.3
	MeOH-H_2O gravimetric reference solution, ~0.5%	0.5
	Czech C-18 stationary phase, laboratory conditions	0.7 – 0.8
	Tecophilic SP-60D-60 (Polyurethane)	0.7 – 1.1
	1% standard material (CRM)	1.0
	ROTH C-18 stationary phase, laboratory conditions	0.9 – 1.2

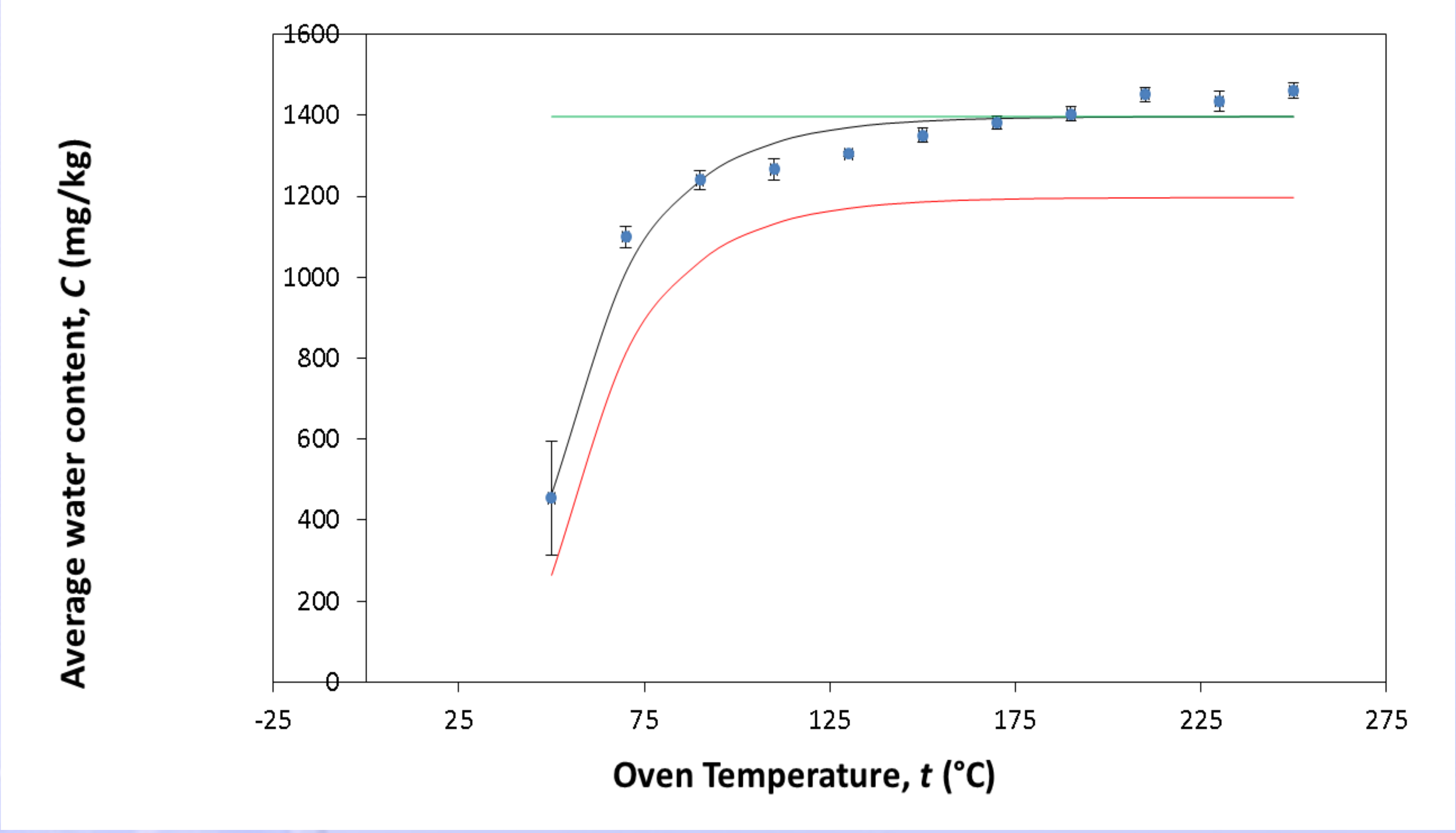
Low water content is more interesting and also more problematic!

Example: polymer (polymorph)

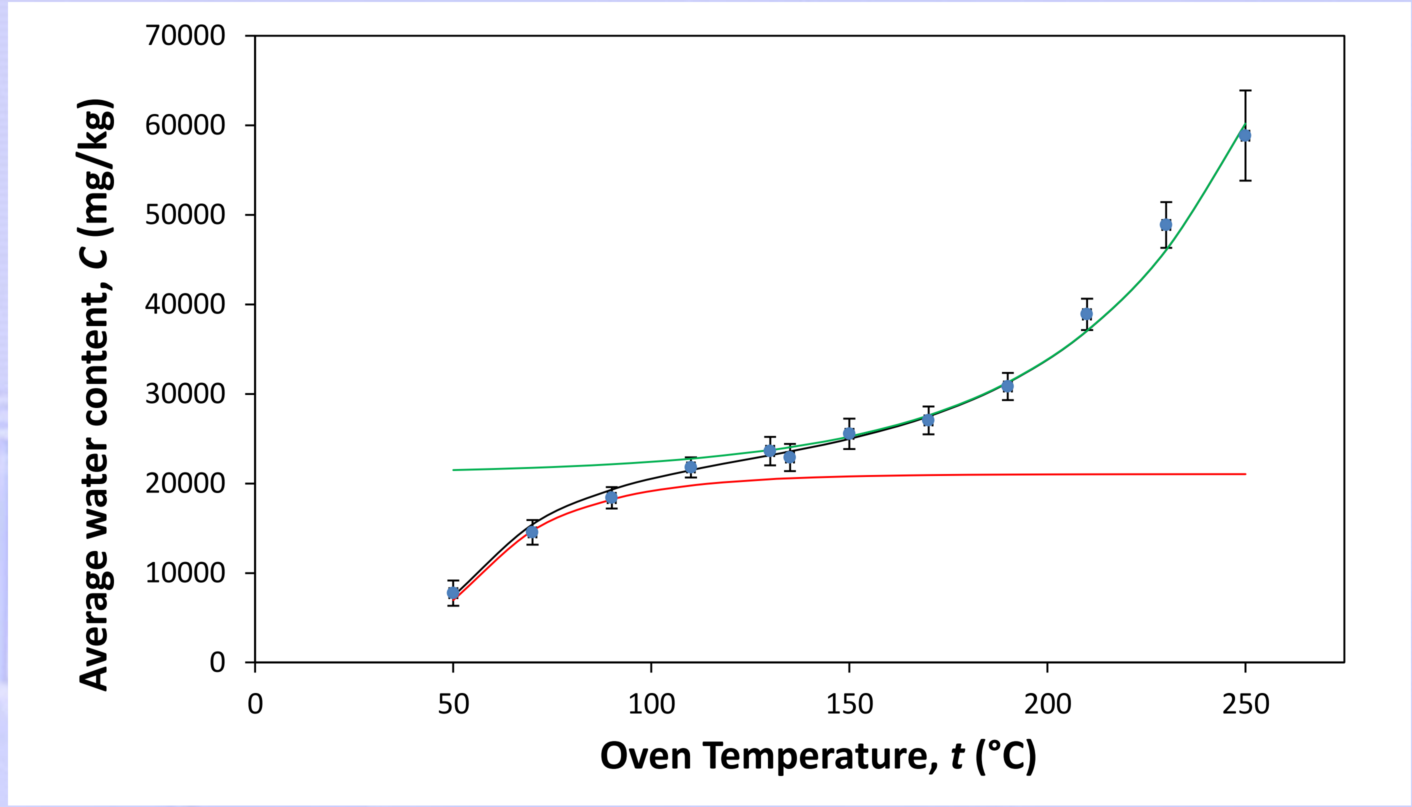


Parameter	Value
Plateau, C0:	1221
Lower offset, a1:	5817
Lower shape, b1x10(	37.22
Higher offset, 1/a2:	10.39
Higher shape, b2x1(	36.95

Example: polymer (polymorph)

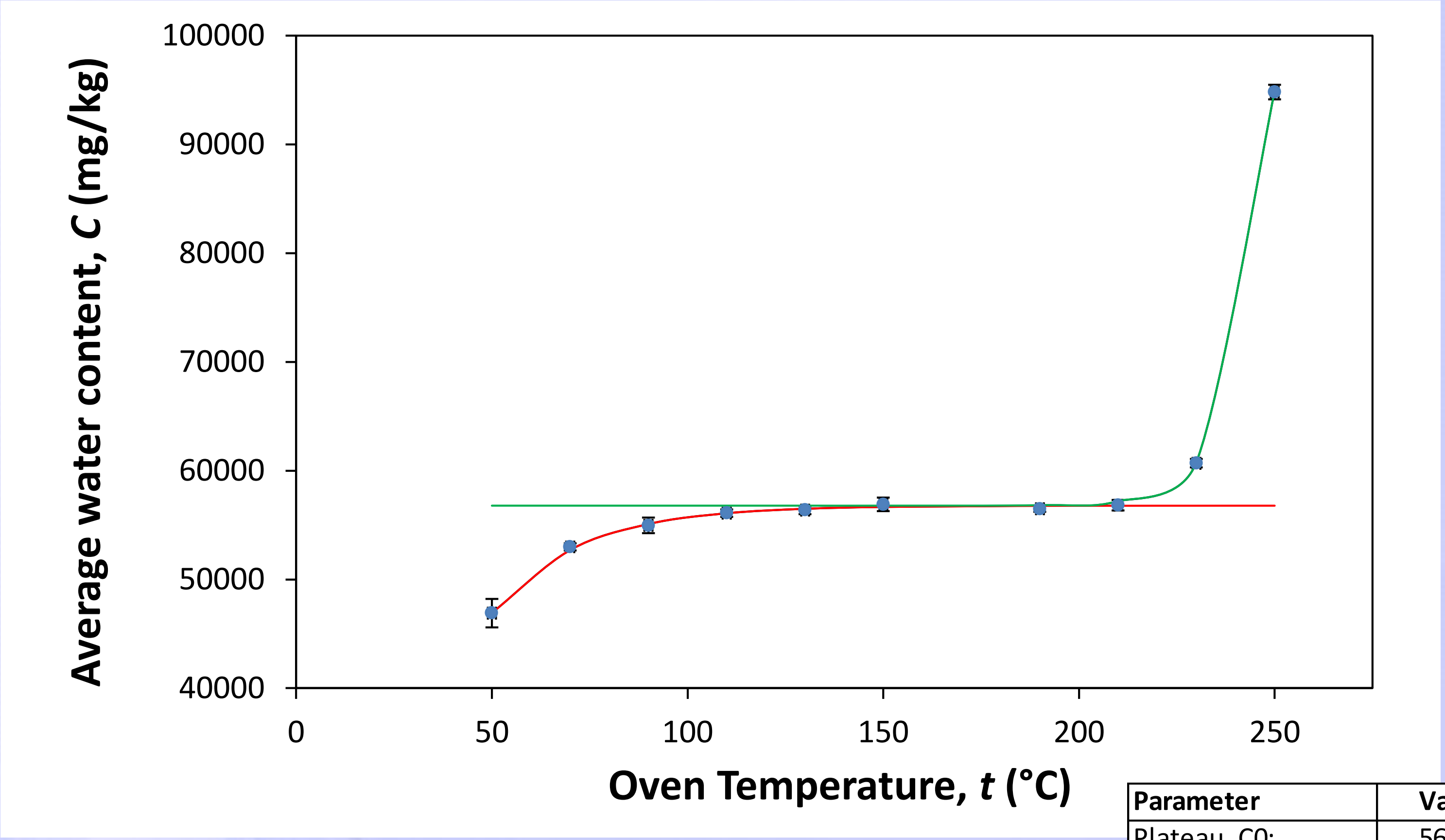


Example: meat bone meal



Parameter	Value
Plateau, C0:	21047
Lower offset, a1:	103885
Lower shape, b1x10(	39.98
Higher offset, 1/a2:	0.01
Higher shape, b2x1(	22.33

Example: paper



Parameter	Value
Plateau, C0:	56788
Lower offset, a1:	89360
Lower shape, b1x10(	44.08
Higher offset, 1/a2:	45367560
Higher shape, b2x1(	112.72

Potential usefulness of the model

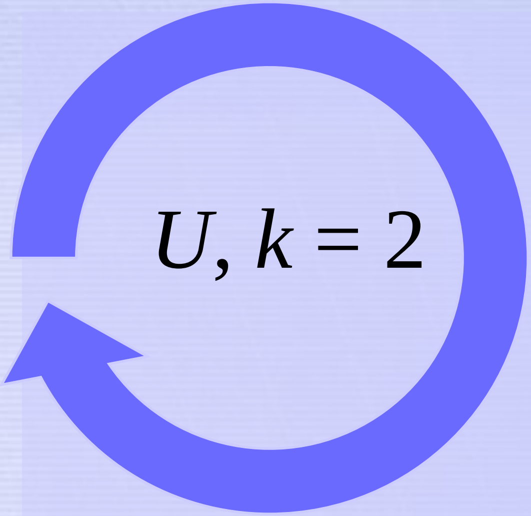
$$C = C_0 - a_1 e^{-b_1 t} + a_2 e^{b_2 t}$$

Usefulness of the model:

- **Elucidating the processes**
- **Finding suitable measurement conditions**
- **Finding water content as C_0 from least squares fitting data**
- **As possible first step in investigating new materials**
- **As routine approach for high-accuracy measurements**

But:

- **Not always straightforward to use**
- **Not necessarily universal**



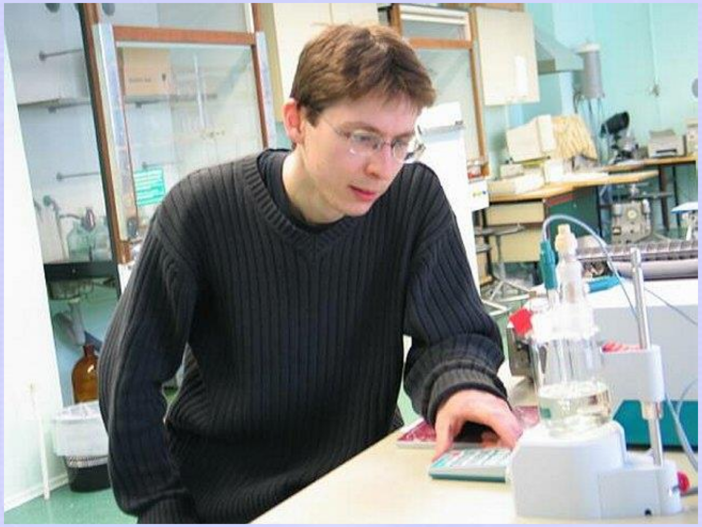
Preliminary measurement uncertainty

- The Nordtest approach was applied
  - Bias component was estimated with a gravimetric reference solution
  - Precision component was estimated using real samples
- Measurement uncertainty estimation was obtained for different measurement situations

Preliminary measurement uncertainty

Relative expanded uncertainty (k = 2) for real samples, using the oven system

	Simple sample	Difficult sample
Low content	2.6 %	(5 .. 27 %)
High content	1.7 %	3.0 %



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Thank you for your attention!

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