STK Annual Meeting 2018, May 15th 2018
Innovation in Thermal Analysis and Calorimetry

AKTS AG
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AKTS-THERMOKINETICS AKTS-THERMAL SAFETY AKTS-SML AKTS-CALISTO

Influence of Polymorphic Transition on the Thermal Behavior of Quasi-Autocatalytically Decomposed Solids

B. Roduit[1], M. Hartmann[1], P. Folly[2], A. Sarbach[2], A. Dejeaifve[3], R. Dobson[3], K. Kurko[4]

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Scale-up of Thermal Behavior of Quasi-Autocatalytically Decomposed Solids: How the Phase Transition and Melting can Influence the Experimental Workflow

B. Roduit[1], M. Hartmann[1], P. Folly[2], A. Sarbach[2], A. Dejeaifve[3], R. Dobson[3], K. Kurko[4]

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To say it in another way:

based on few thermoanalytical experiments carried out
in high pressure sealed crucibles
with few mg sample,
can one predict the thermal behavior
of few kg sample ?

mg

?

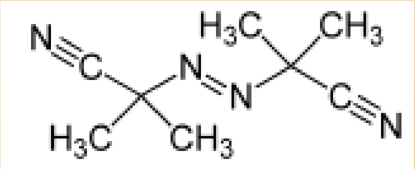
kg

For the illustration of my remarks

I will use as example

the results of a study of the thermal behavior of

AIBN (Azobisisobutyronitrile)

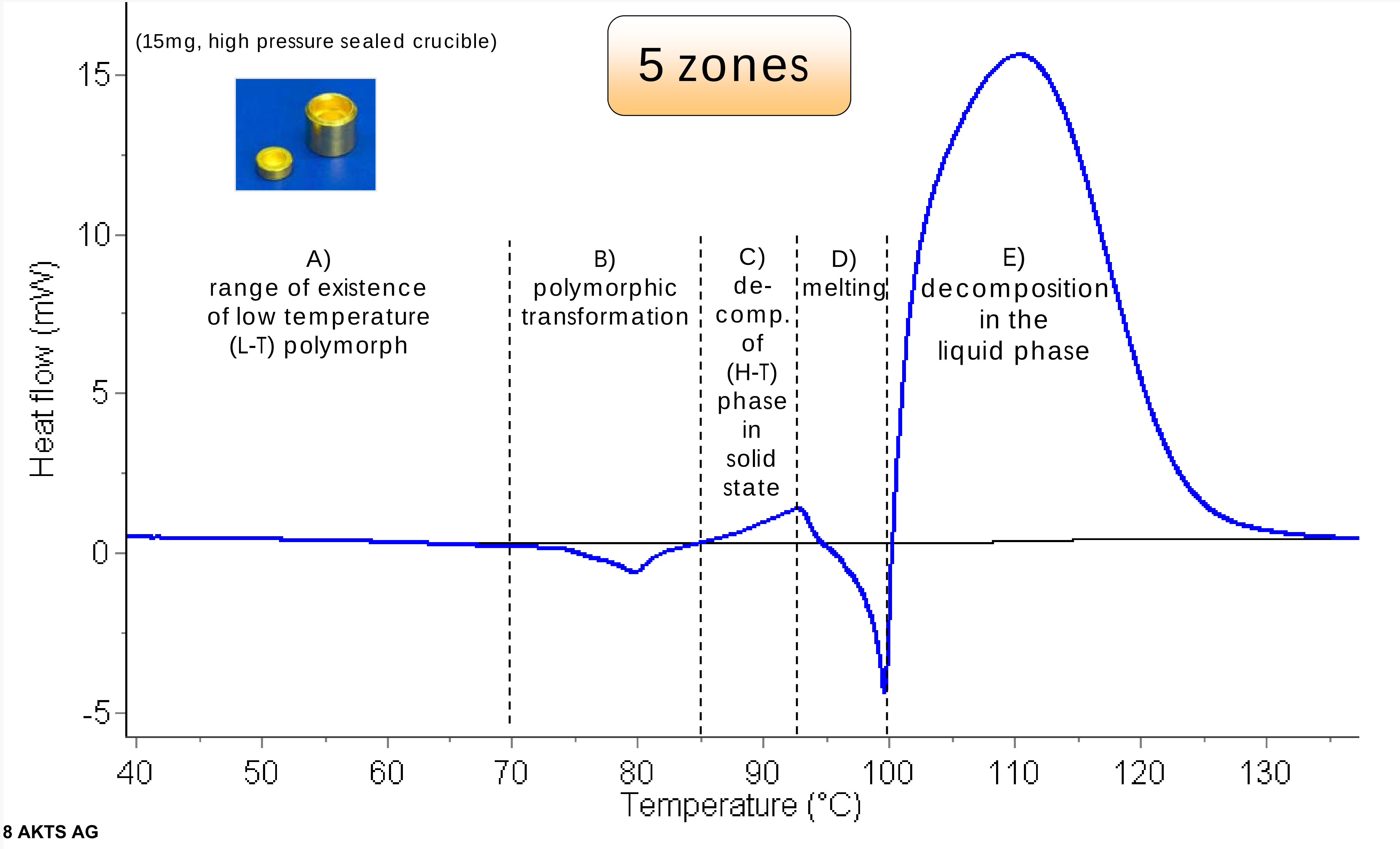


The applied method will be based on kinetic and heat balance approaches.

Why AIBN?

Why KINETICS?

DSC traces of AIBN recorded by DSC at 2 $Kmin^{-1}$



Why AIBN?

Because
it decomposes exothermally,
and may be potentially dangerous during storage
Additionally:
(i) it has a polymorphic transition and melting before decomposition
(ii) and its decomposition is quasi-autocatalytic.

Why KINETICS?

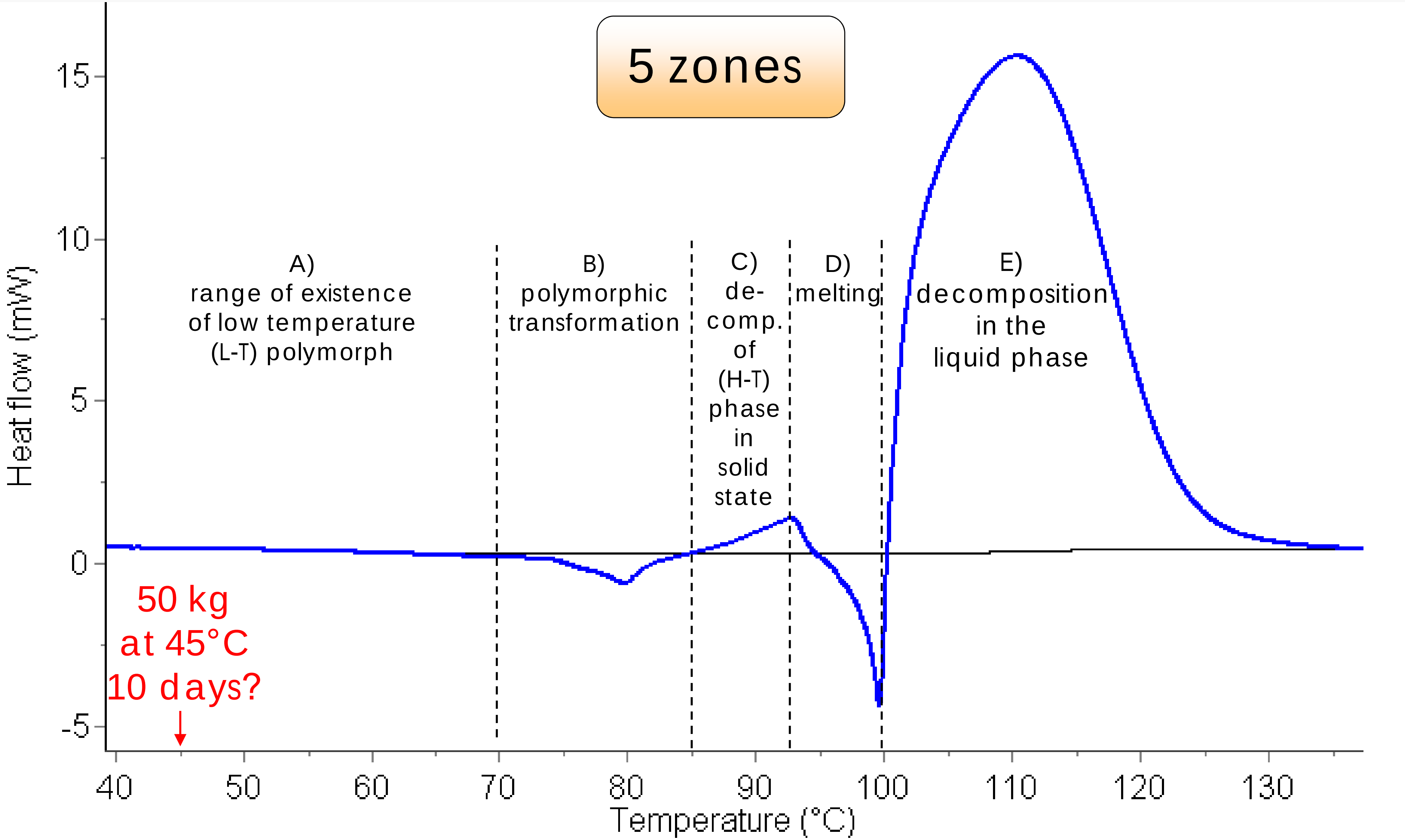
Because with small amount of material
one can determine the rate of heat evolution
which can lead to thermal hazard of larger amount of substance.

Based on few heat flow experiments carried out
with few mg of AIBN,

is it possible to predict

if 50 kg of AIBN
at surrounding temperature of 45°C
will be stable during a laps period of10 days?

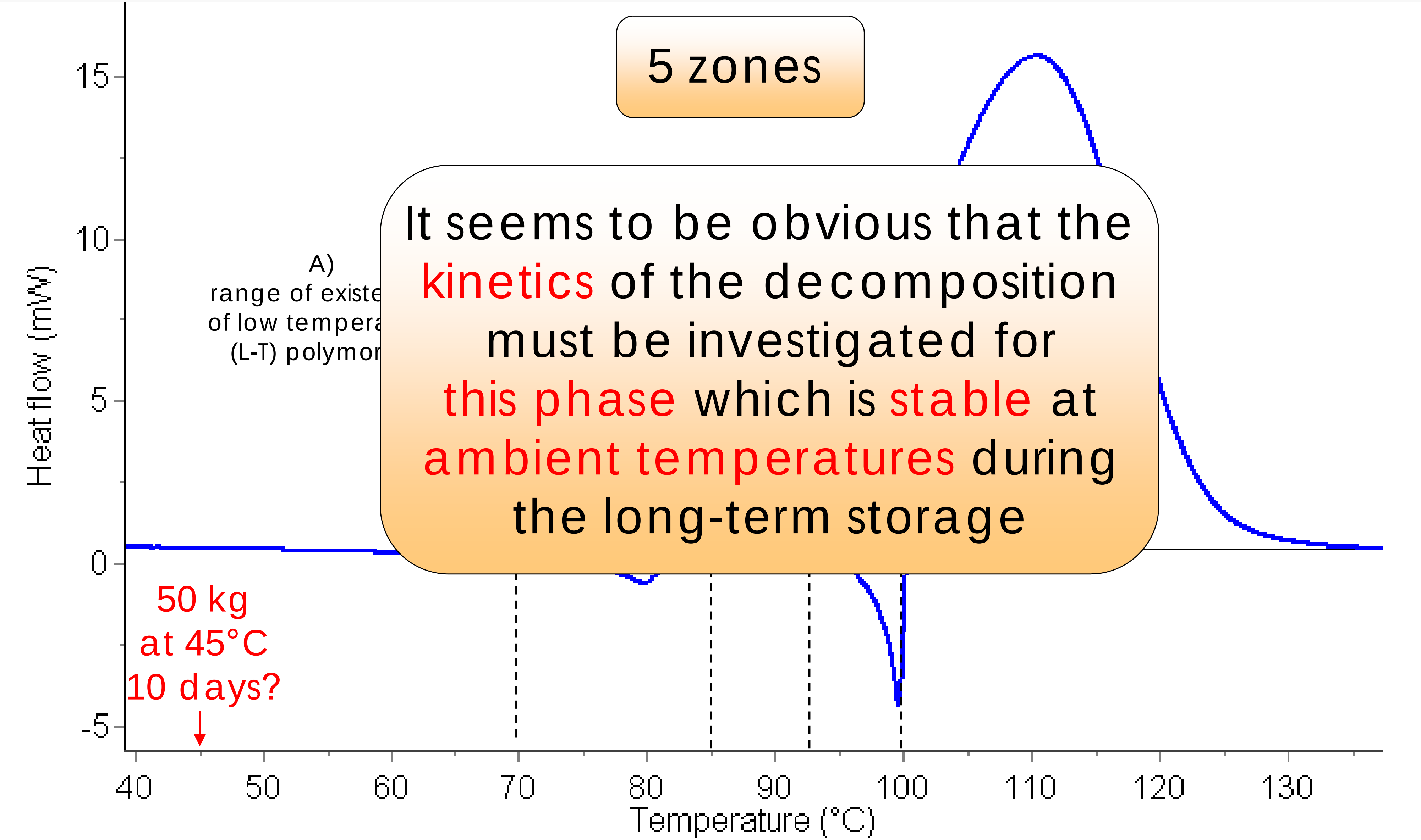
DSC traces of AIBN recorded by DSC at 2 $K min^{-1}$



(15mg, high pressure sealed crucible)

DSC traces of AIBN recorded by DSC at 2 Kmin^{-1}

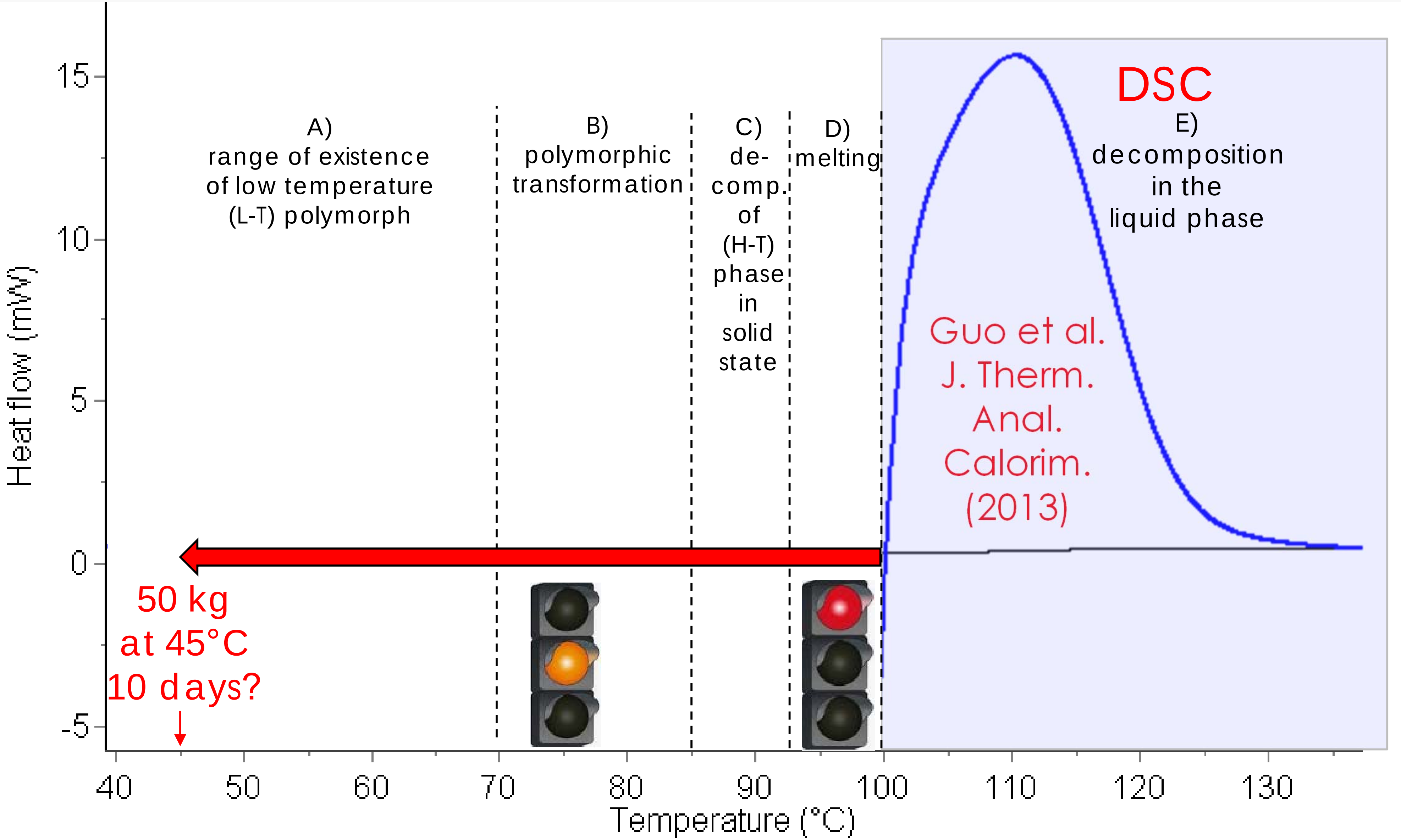
5 zones



It seems to be obvious that the kinetics of the decomposition must be investigated for this phase which is stable at ambient temperatures during the long-term storage

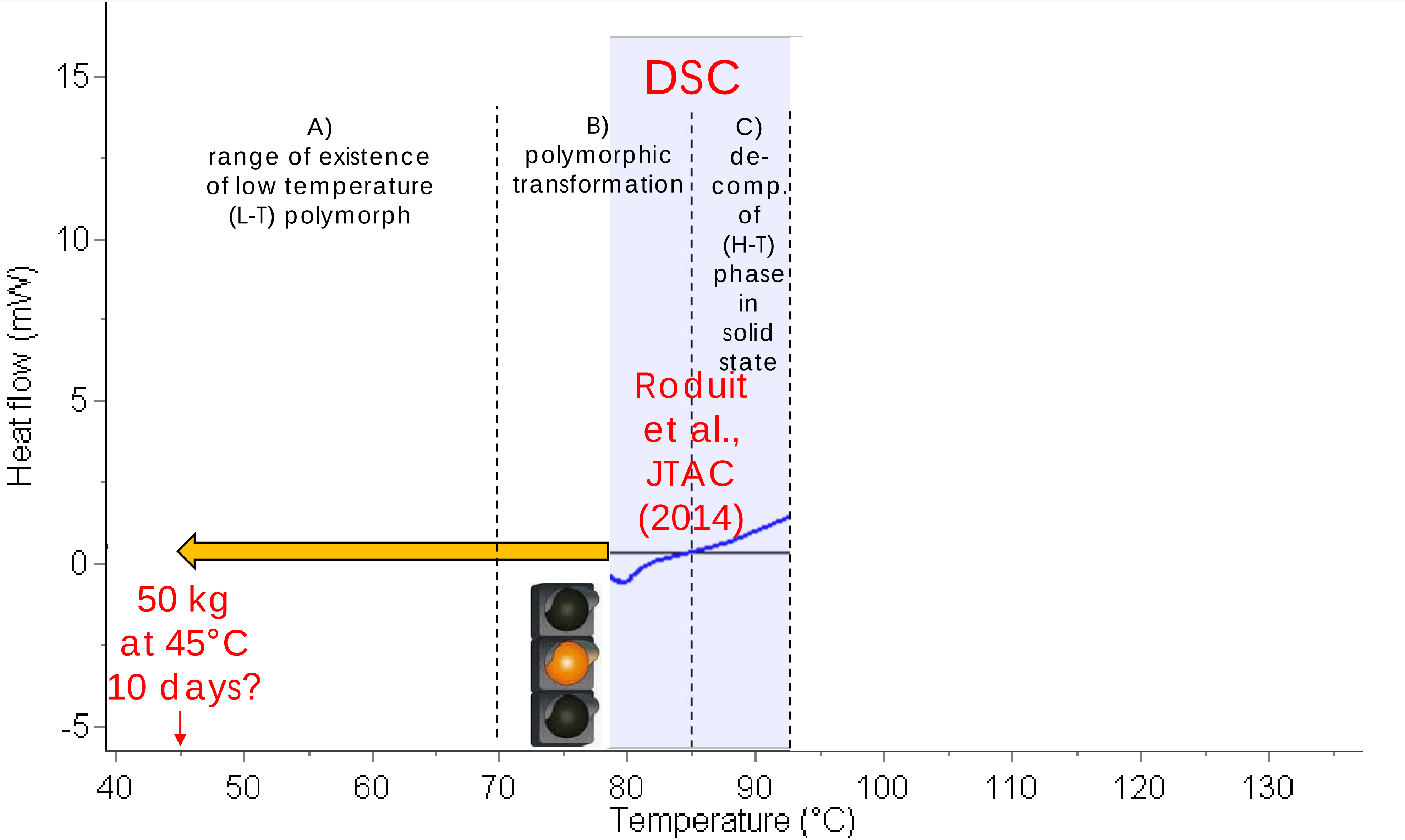
(15mg, high pressure sealed crucible)

DSC traces of AIBN recorded by DSC at 2 Kmin^{-1}



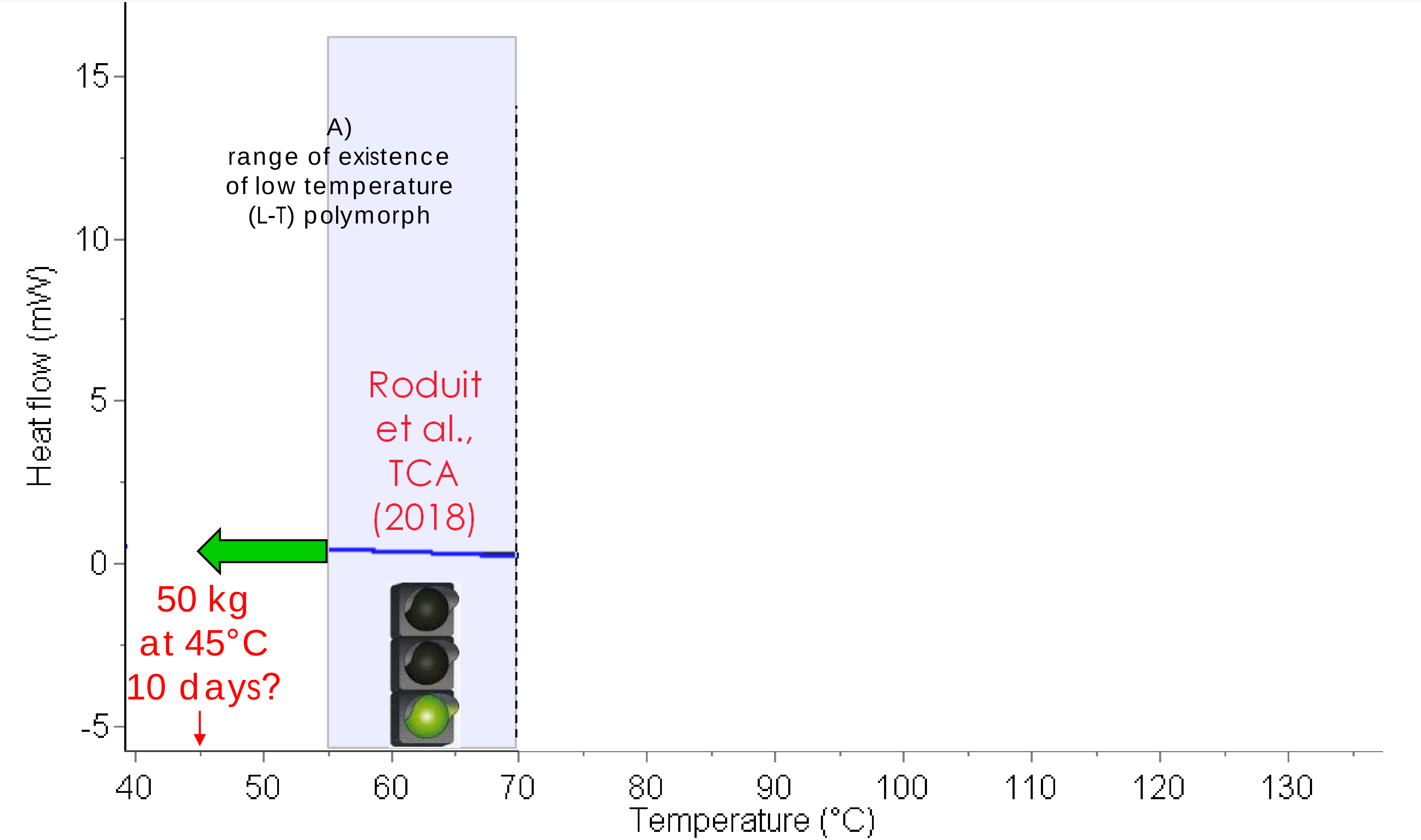
(15mg, high pressure sealed crucible)

DSC traces of AIBN recorded by DSC at 2 Kmin^{-1}



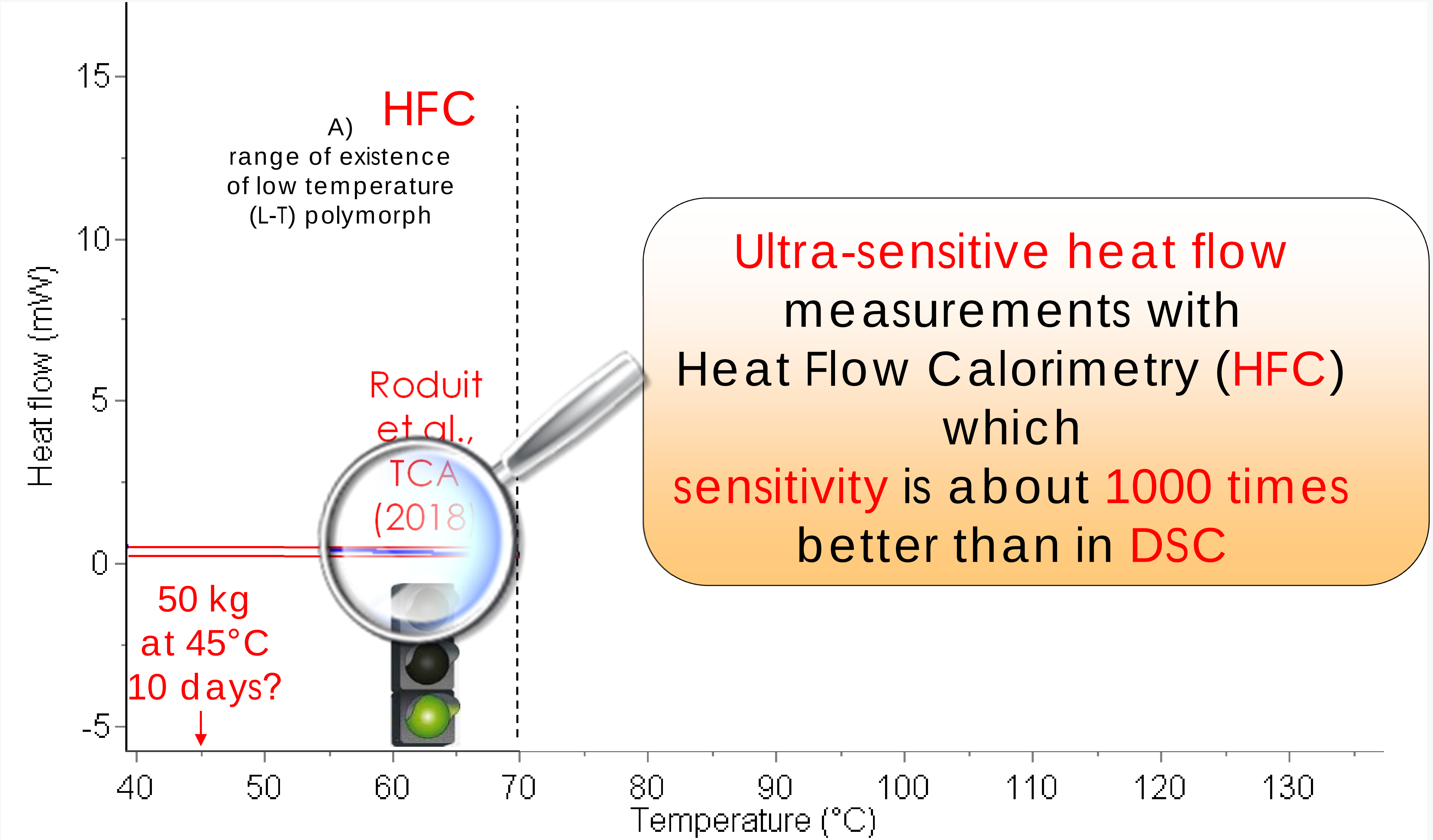
(15mg, high pressure sealed crucible)

DSC traces of AIBN recorded by DSC at 2 Kmin-1



(15mg, high pressure sealed crucible)

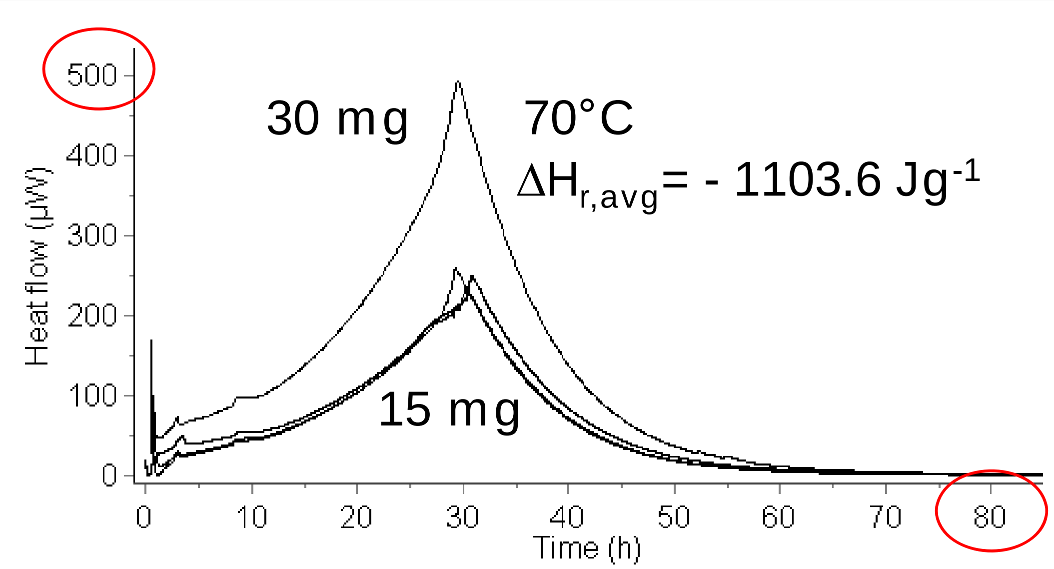
DSC traces of AIBN recorded by DSC at 2 Kmin^{-1}



Ultra-sensitive heat flow measurements with Heat Flow Calorimetry (HFC) which sensitivity is about 1000 times better than in DSC

(15mg, high pressure sealed crucible)

Heat Flow Calorimetry (HFC) traces of AIBN recorded at 55, 60, 65 and 70°C with the Thermal Activity Monitor (TAM)



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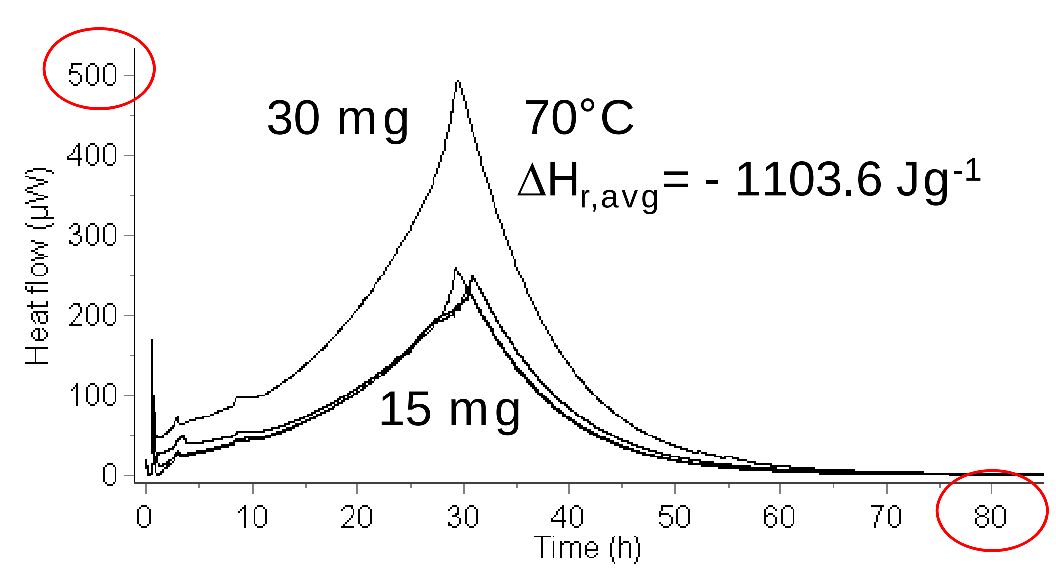

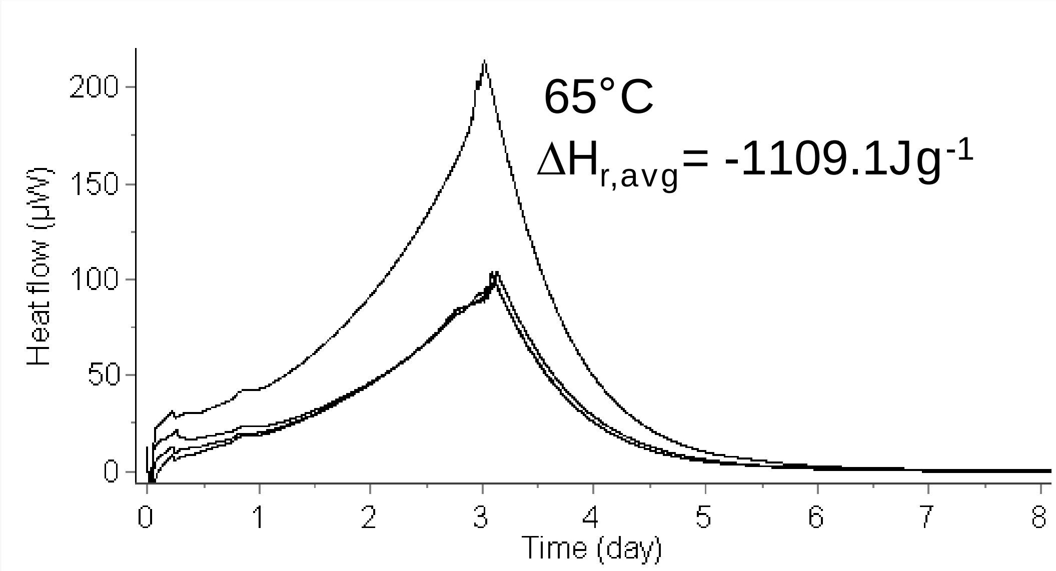

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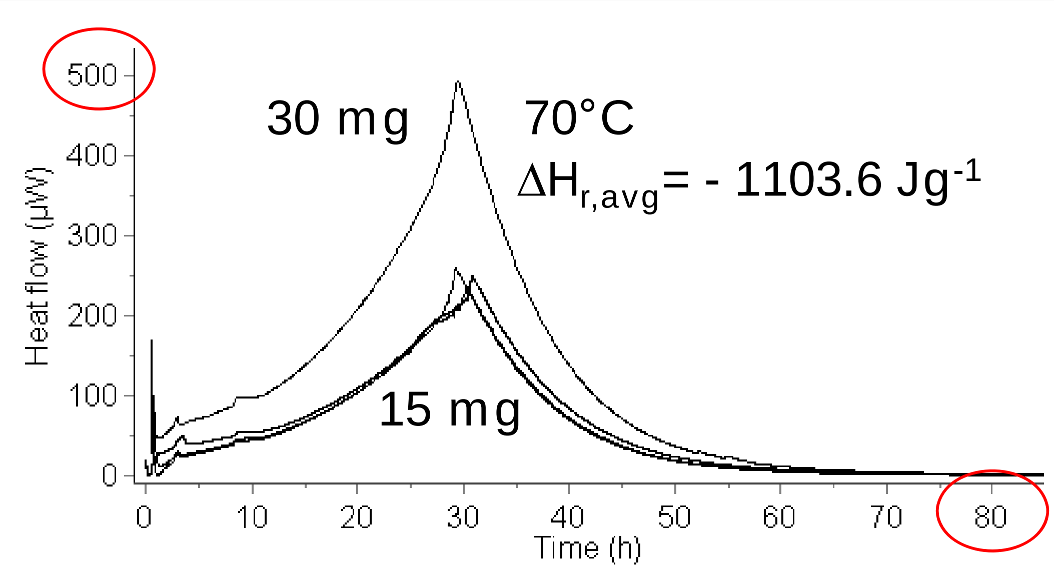

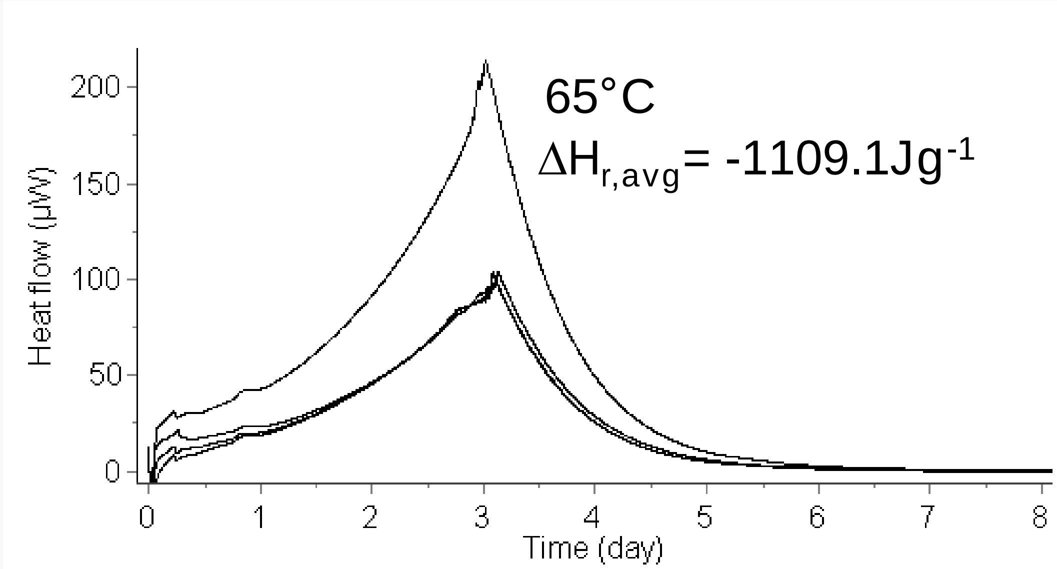

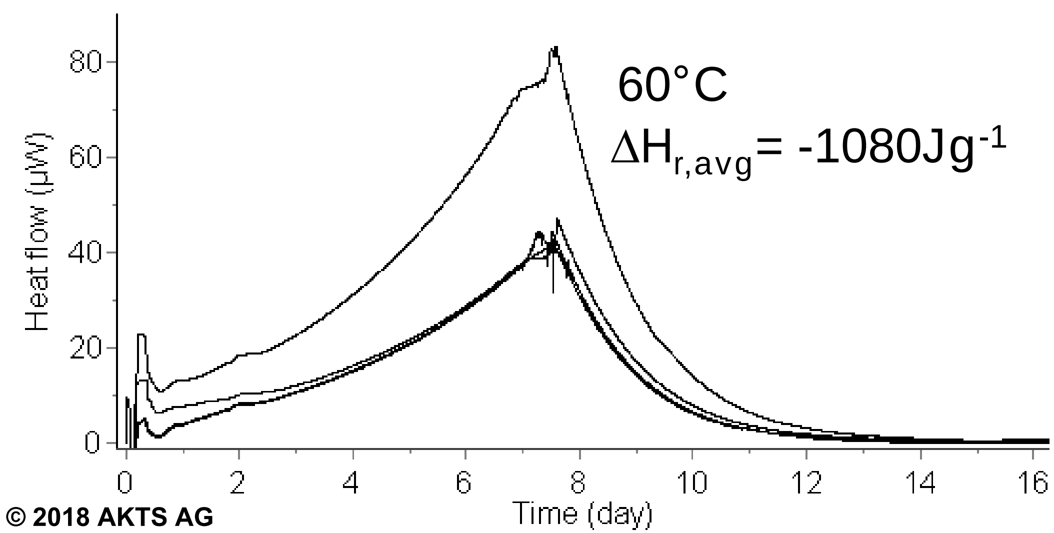

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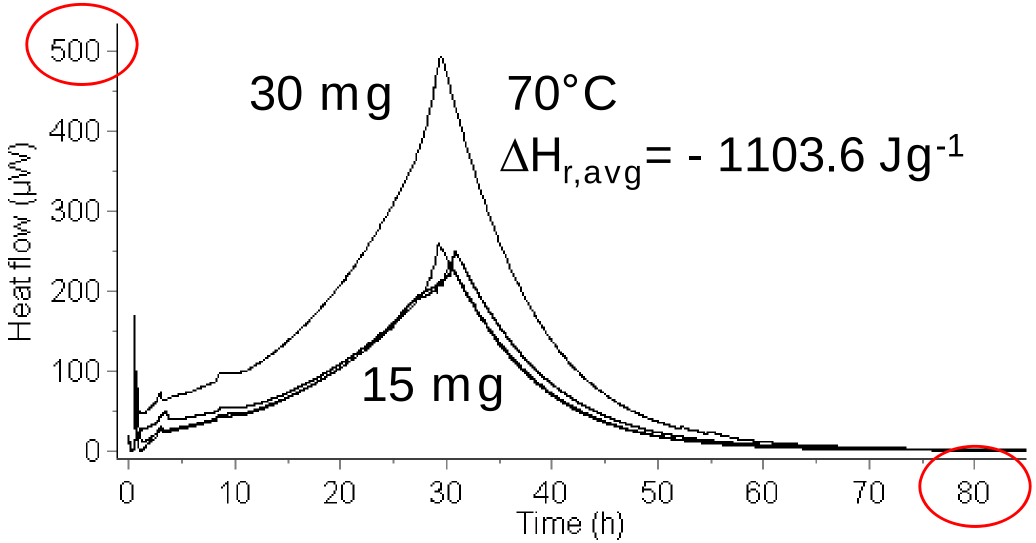
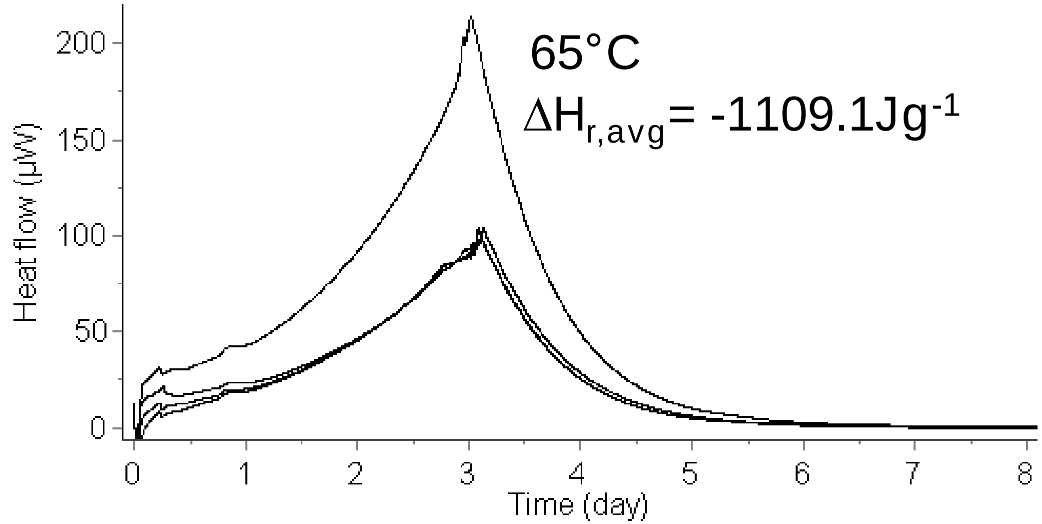
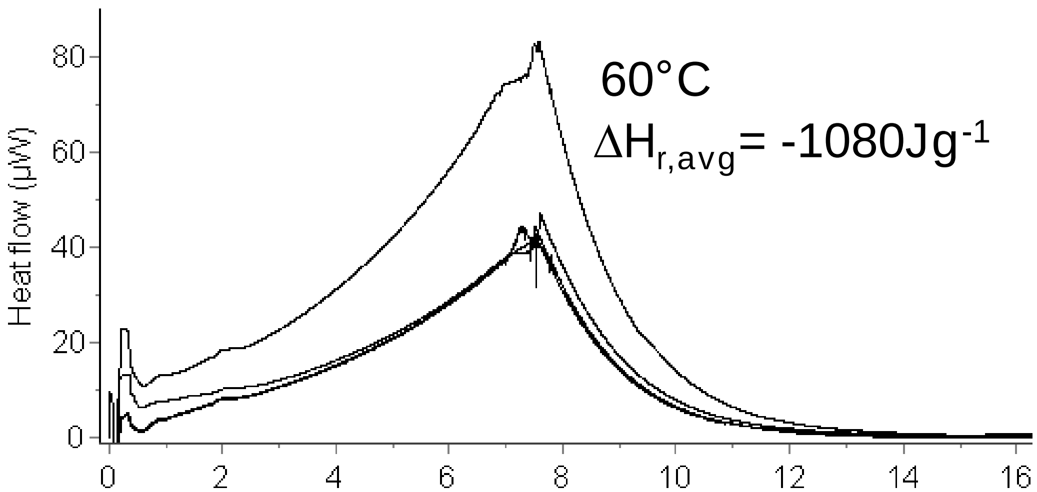
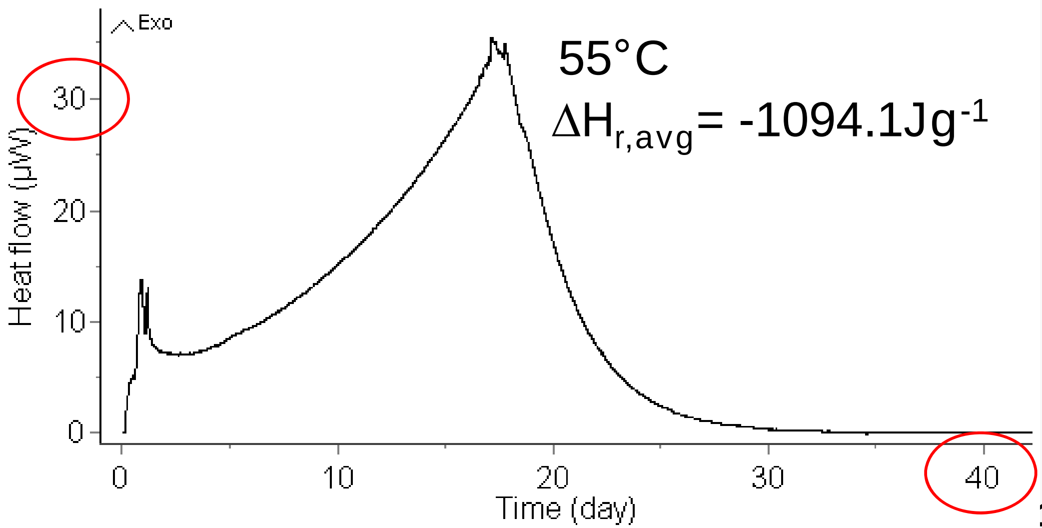


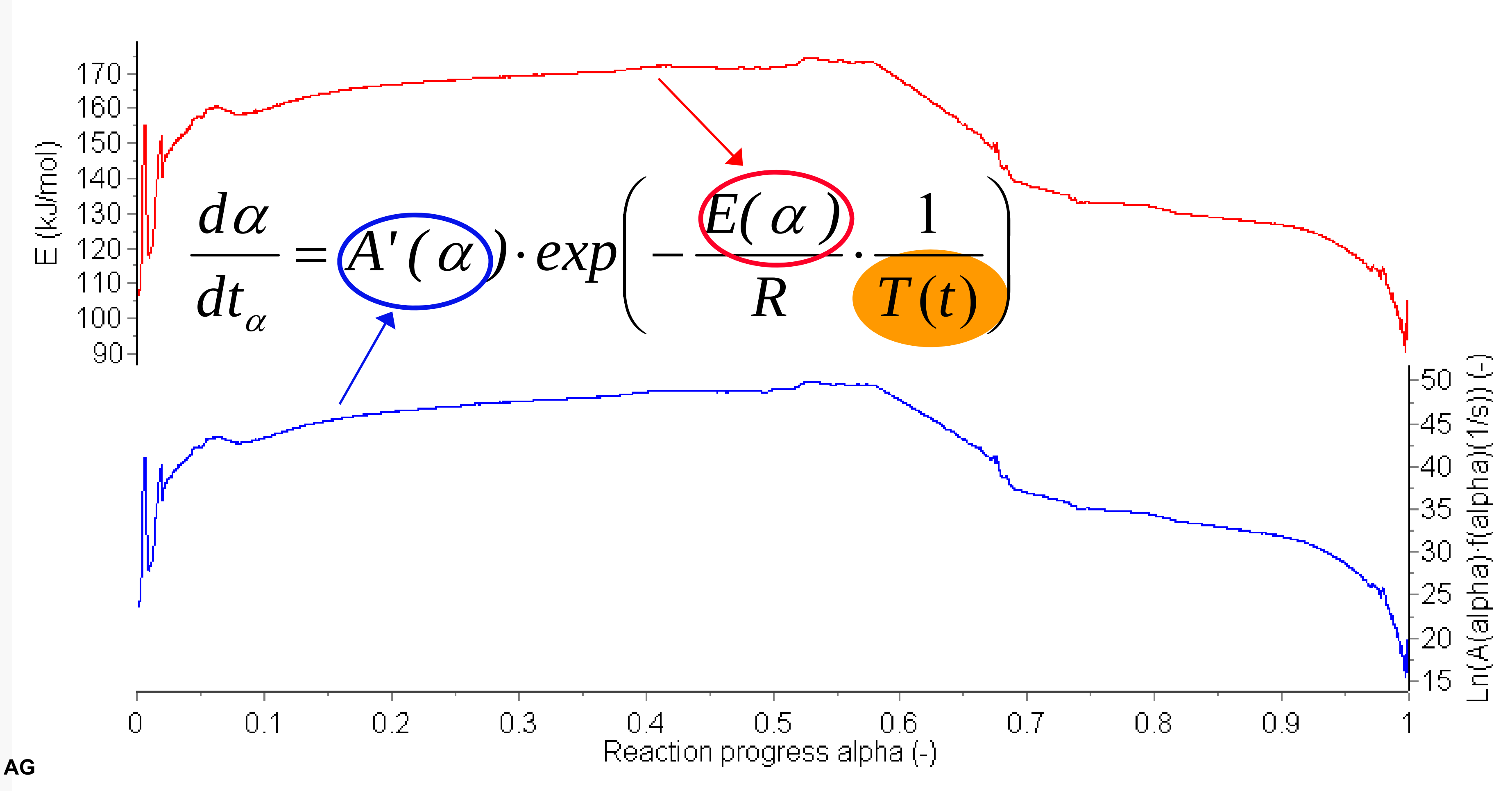






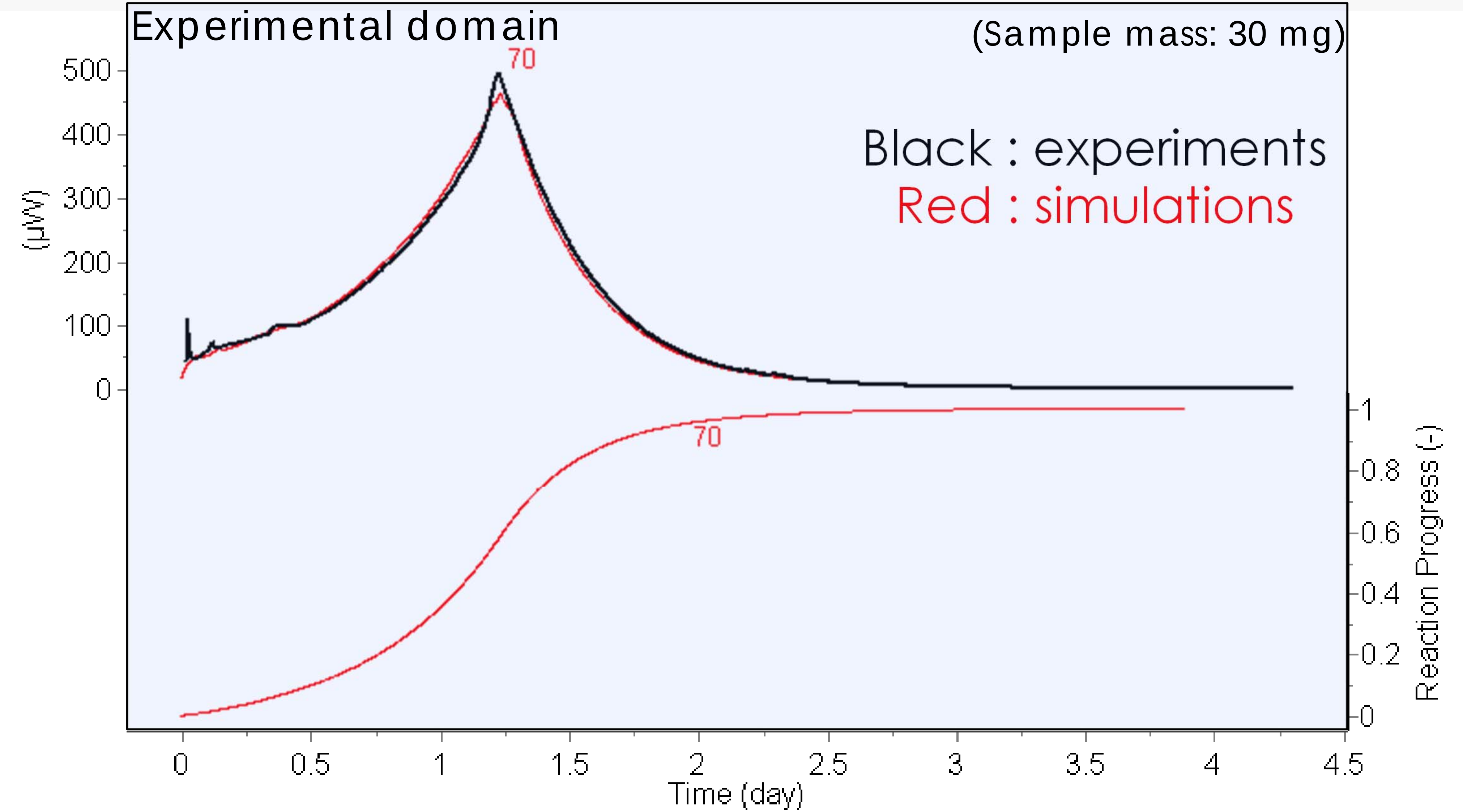
The kinetic parameters were calculated by the differential isoconversional kinetic analysis.

Activation energy $E(\alpha)$ and $\{A(\alpha) f(\alpha)\}$ of AIBN decomposition as a function of the reaction progress α calculated from HFC traces of AIBN recorded at 55, 60, 65 and 70°C.



$$\frac{d\alpha}{dt_\alpha} = A'(\alpha)\cdot \exp\left(-\frac{E(\alpha)}{R}\cdot\frac{1}{T(t)}\right)$$

Having kinetic parameters of the reaction we can predict the rate of the decomposition of AIBN at any temperature.



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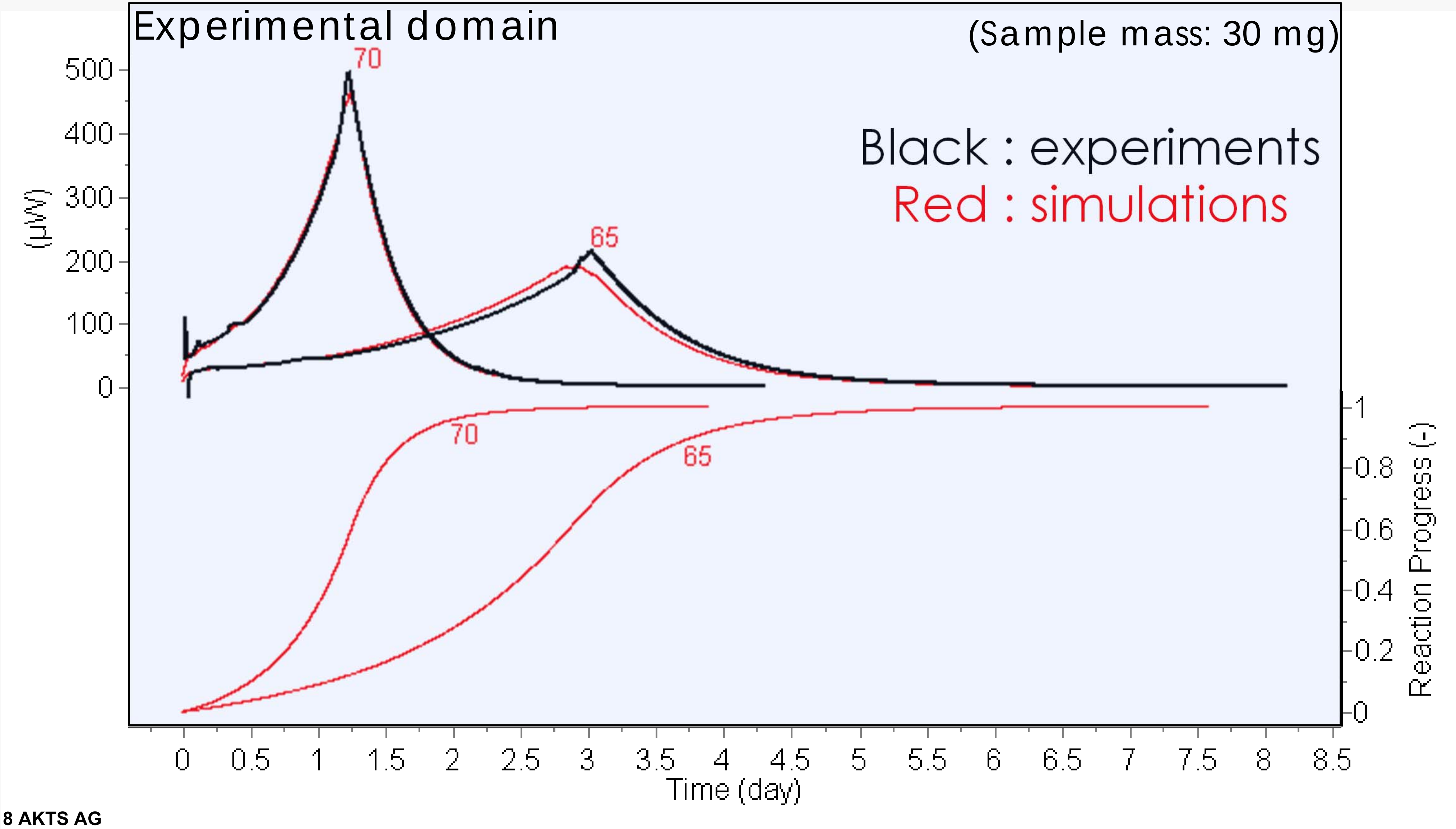

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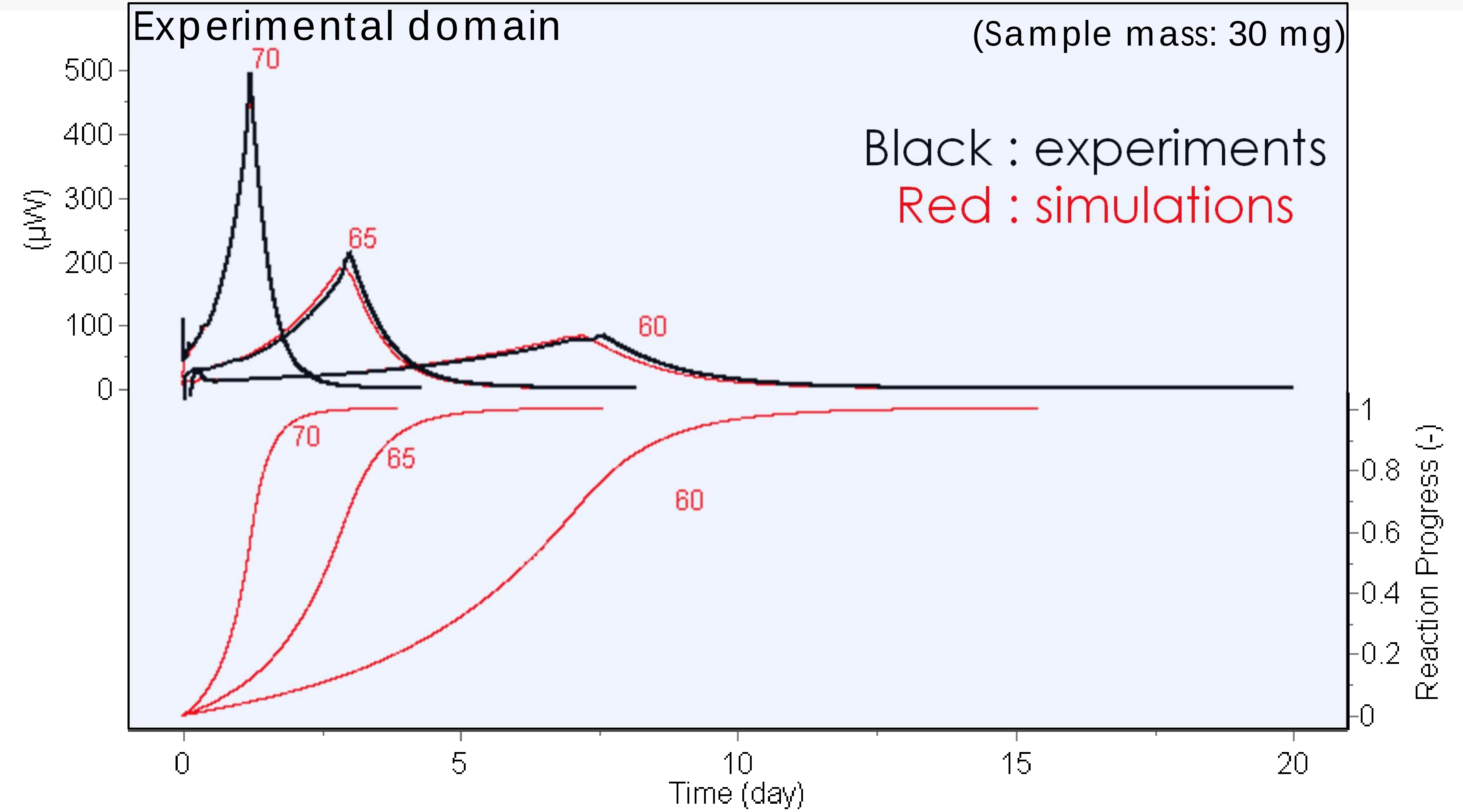

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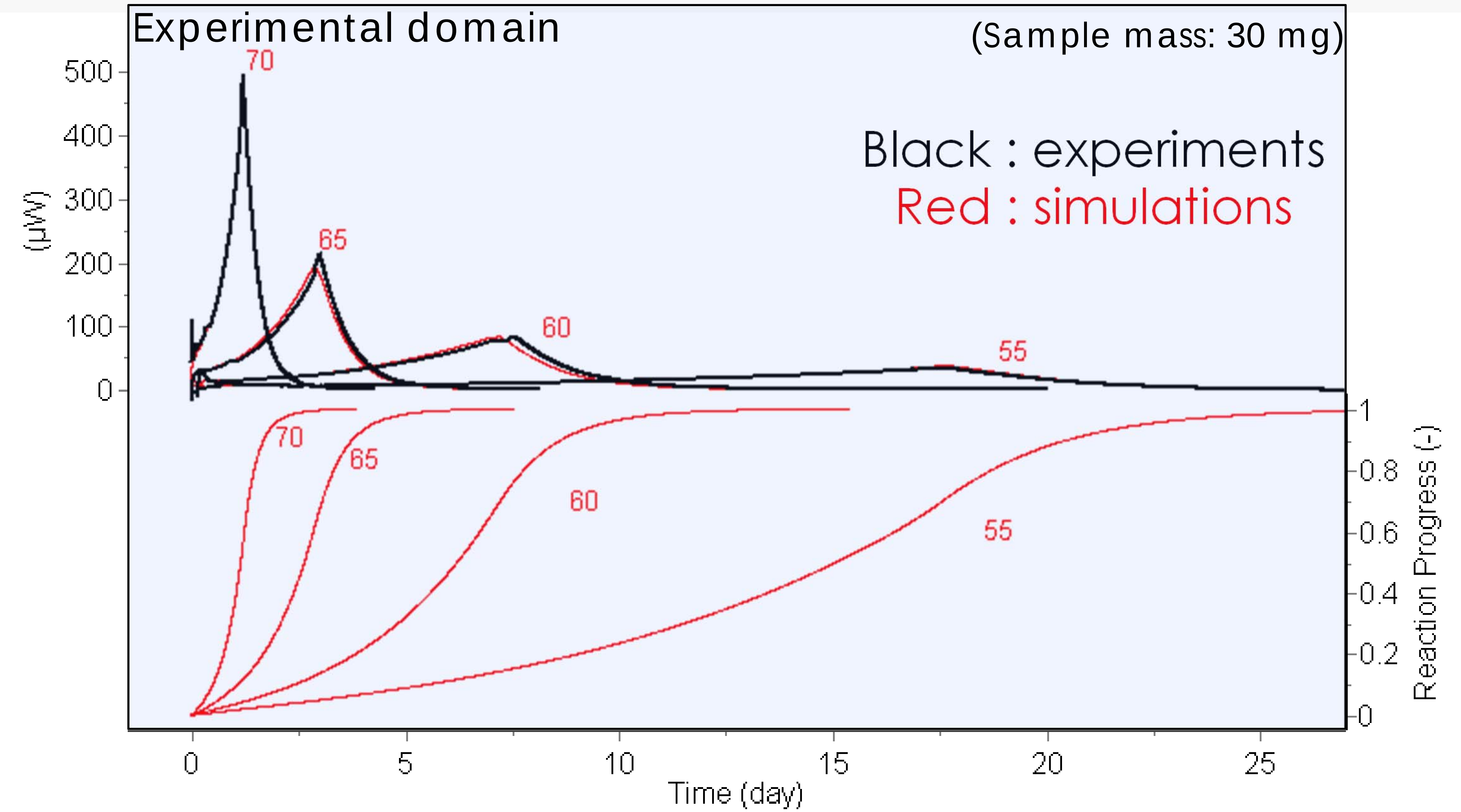

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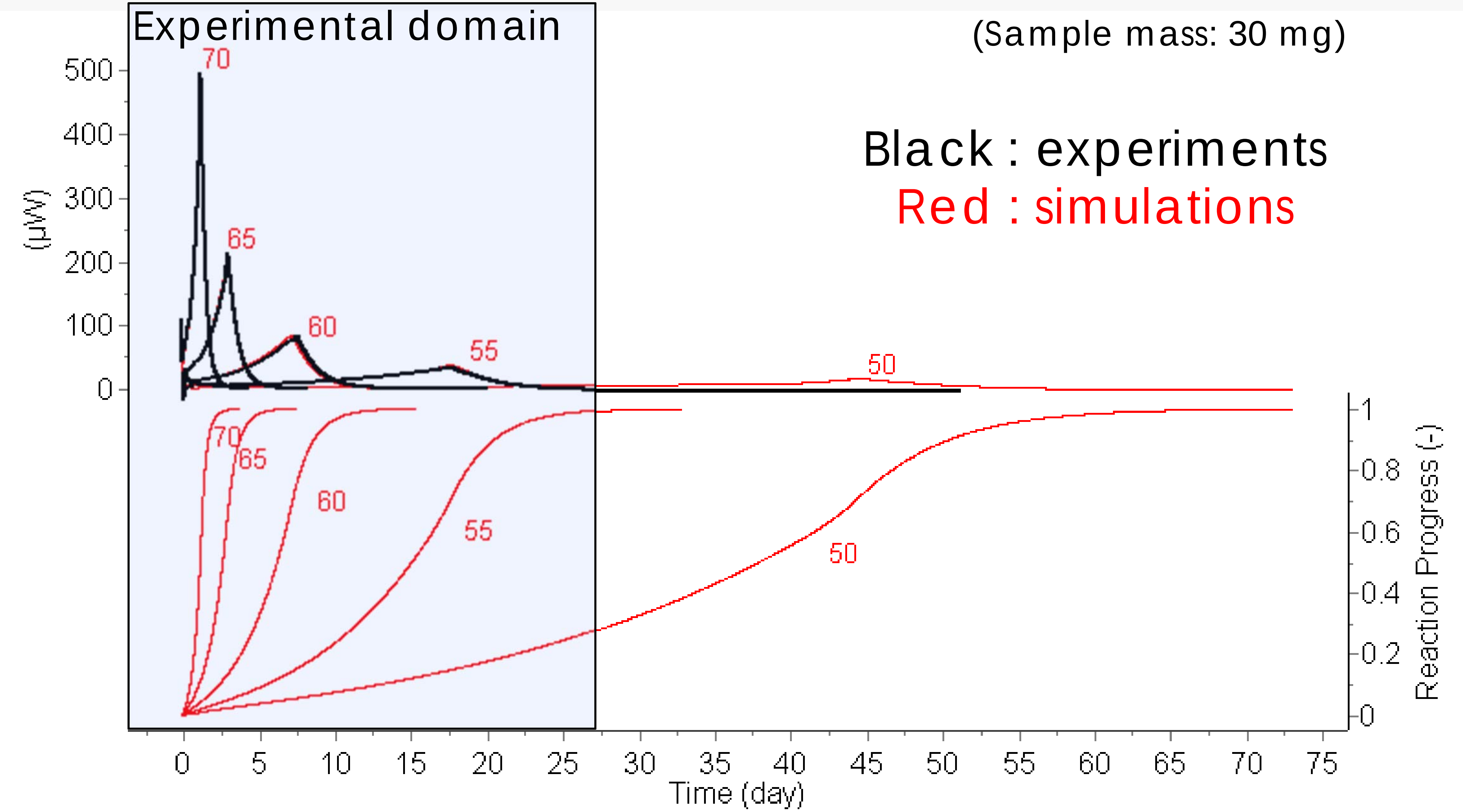

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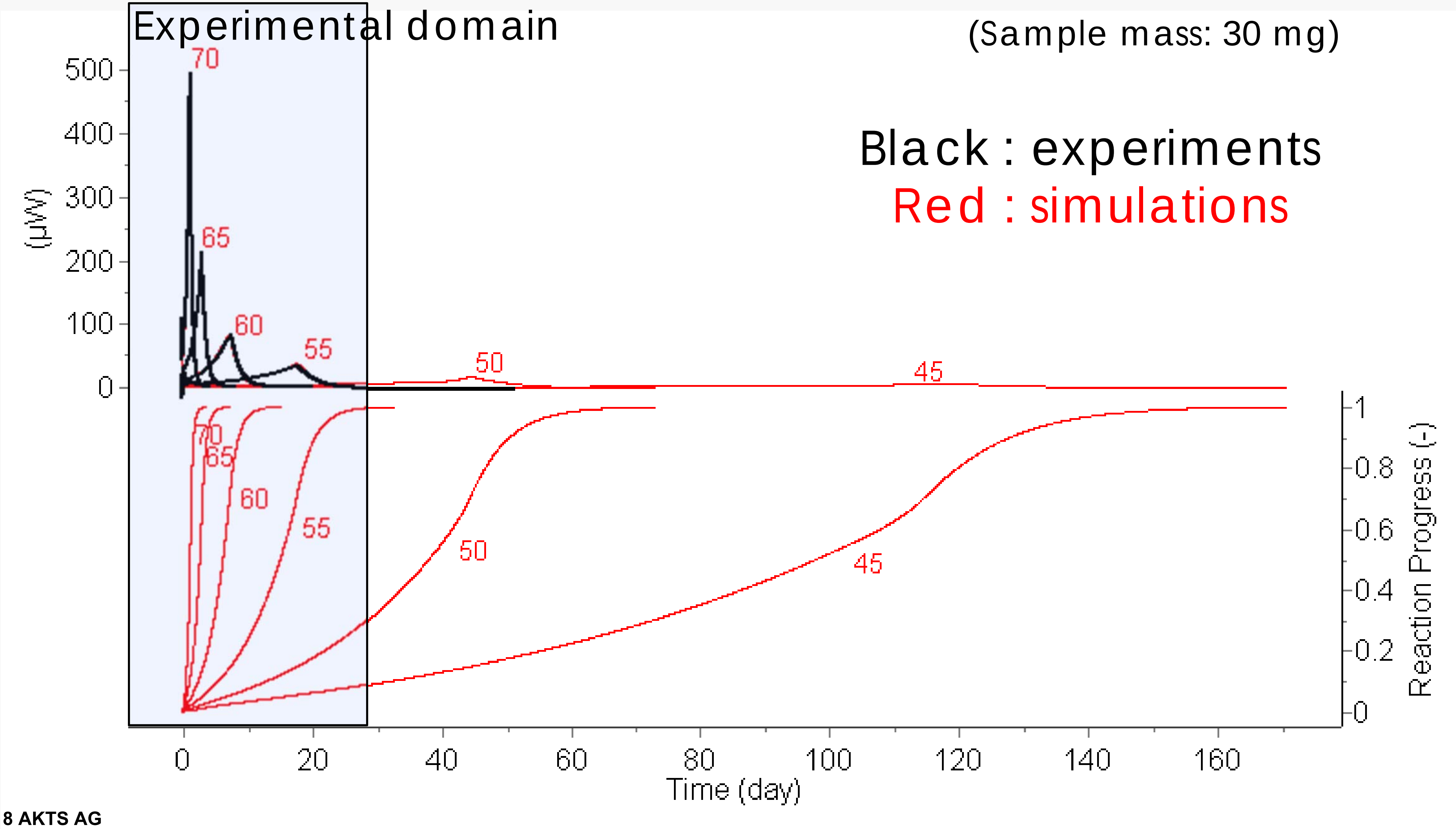


The kinetic parameters are
the same for the 1mg,1g or 1kg sample.

But for scale-up of HFC results,
knowledge of the kinetics is one prerequisite only.
The second one, also very important is
the correct heat balance in the system.

Why?

The kinetic parameters are
the same for the 1mg,1g or 1kg sample.

But for scale-up of HFC results,
knowledge of the kinetics is one prerequisite only.
The second one, also very important is
the correct heat balance in the system.

Because for samples with larger mass the heat cannot be fully exchanged with an environment (as during HFC) what may result in increase of the temperature of the samples and the thermal runaway.

Kinetic parameters and correct heat balance

with few
HFC (TAM) experiments
carried out in
mg scale

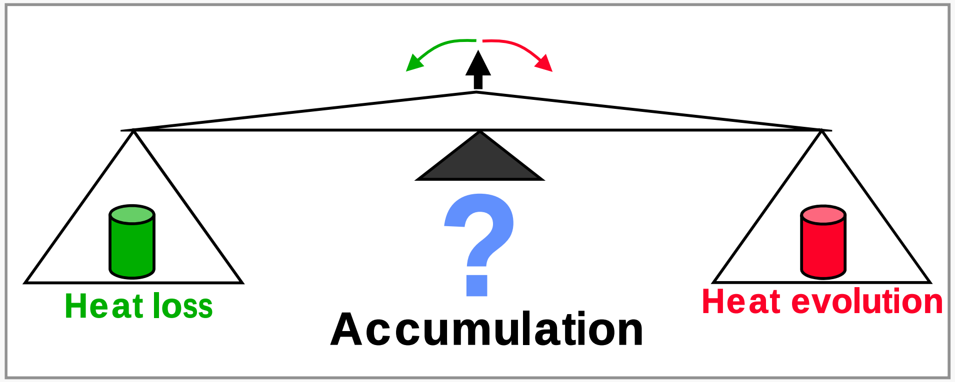
$$\frac{dT}{dt} = f(t) \neq f(m)$$

mg

kinetics

scale-up

kg



with few
HFC (TAM) experiments
carried out in
mg scale

$$\frac{dT}{dt} = f(t) \neq f(m)$$

mg

kinetics

Scale-up

kg

0.127 $W \cdot m^{-1} \cdot K^{-1}$

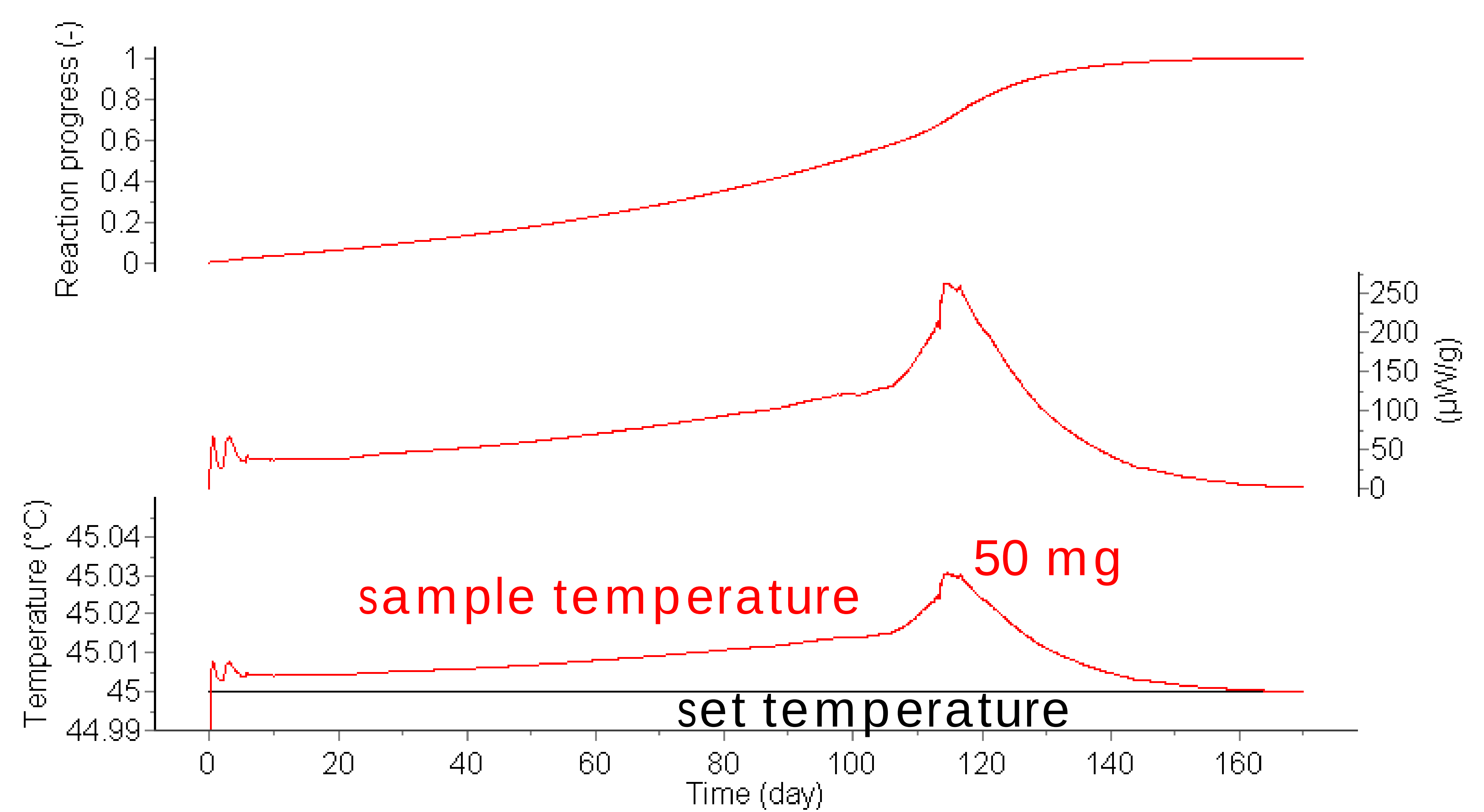
-1097.3 $J \cdot g^{-1}$

$$\frac{dT}{dt} = \frac{\lambda}{\rho Cp}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2}\right) + \frac{-\Delta H_r}{Cp}\frac{d\alpha}{dt}$$

650 $kg \cdot m^{-3}$

1.55 $J \cdot g^{-1} \cdot K^{-1}$

Having kinetic parameters and heat balance we can predict the rate of decomposition of AIBN under any, temperature mode and scale.



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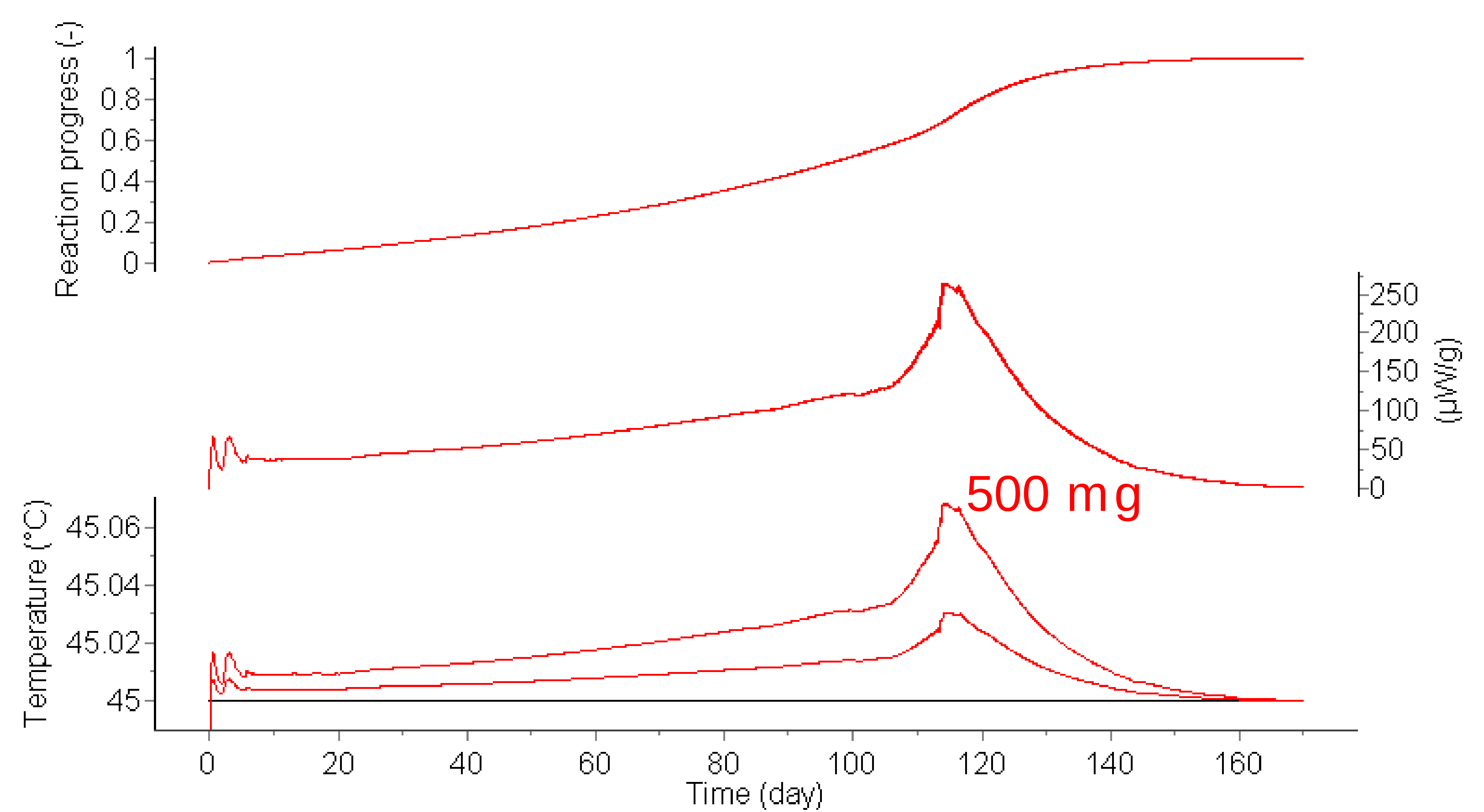

Kinetic parameters and correct heat balance

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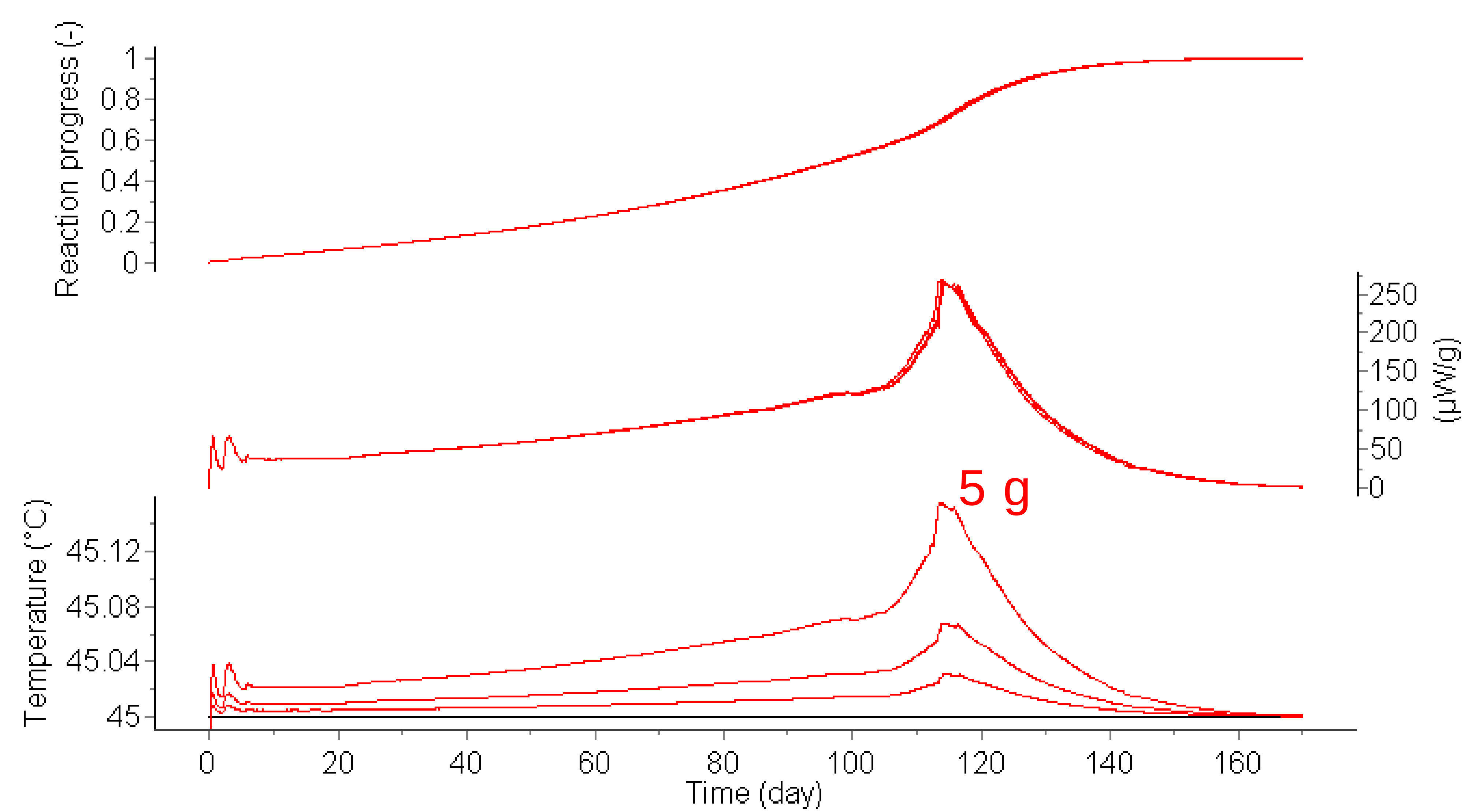

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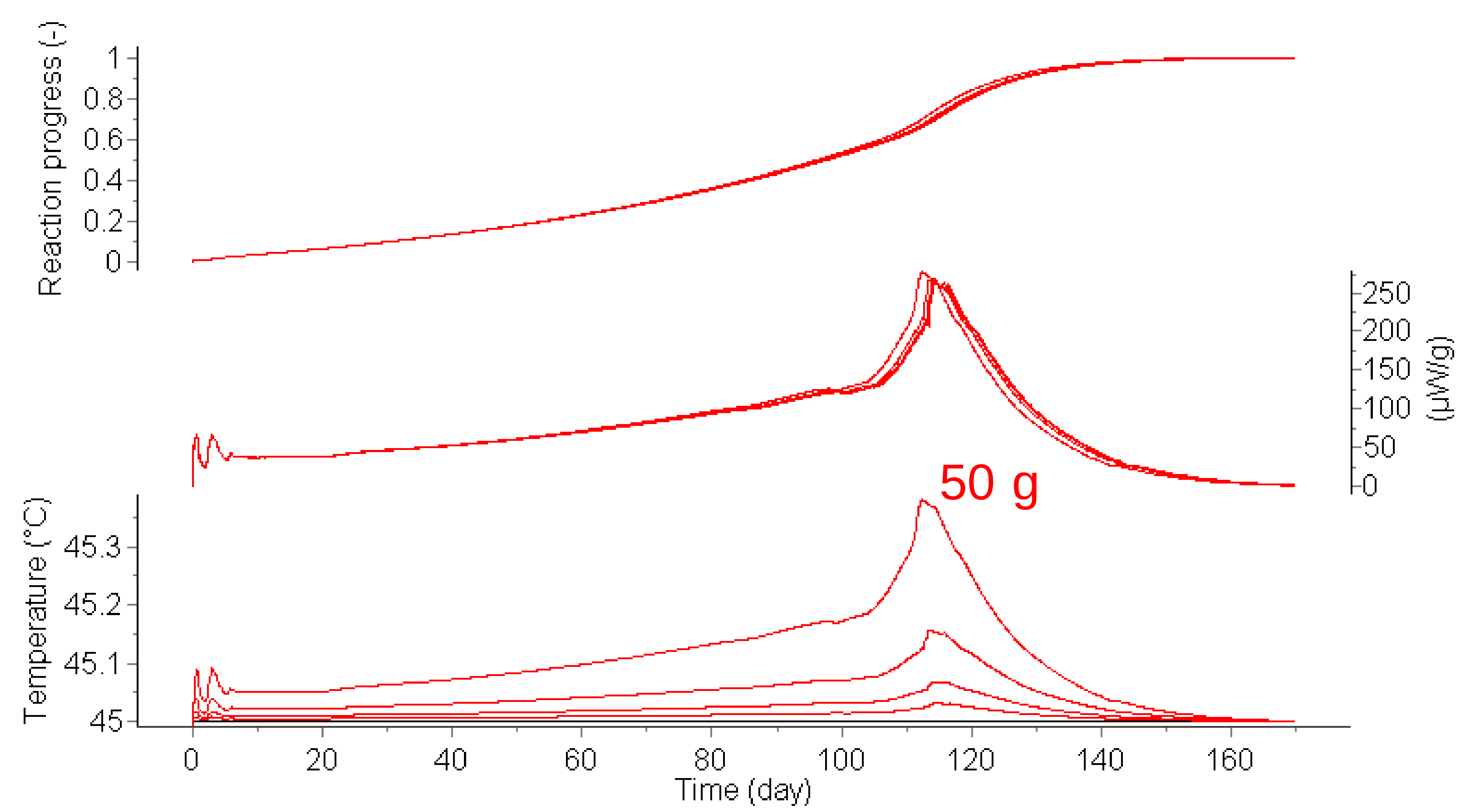

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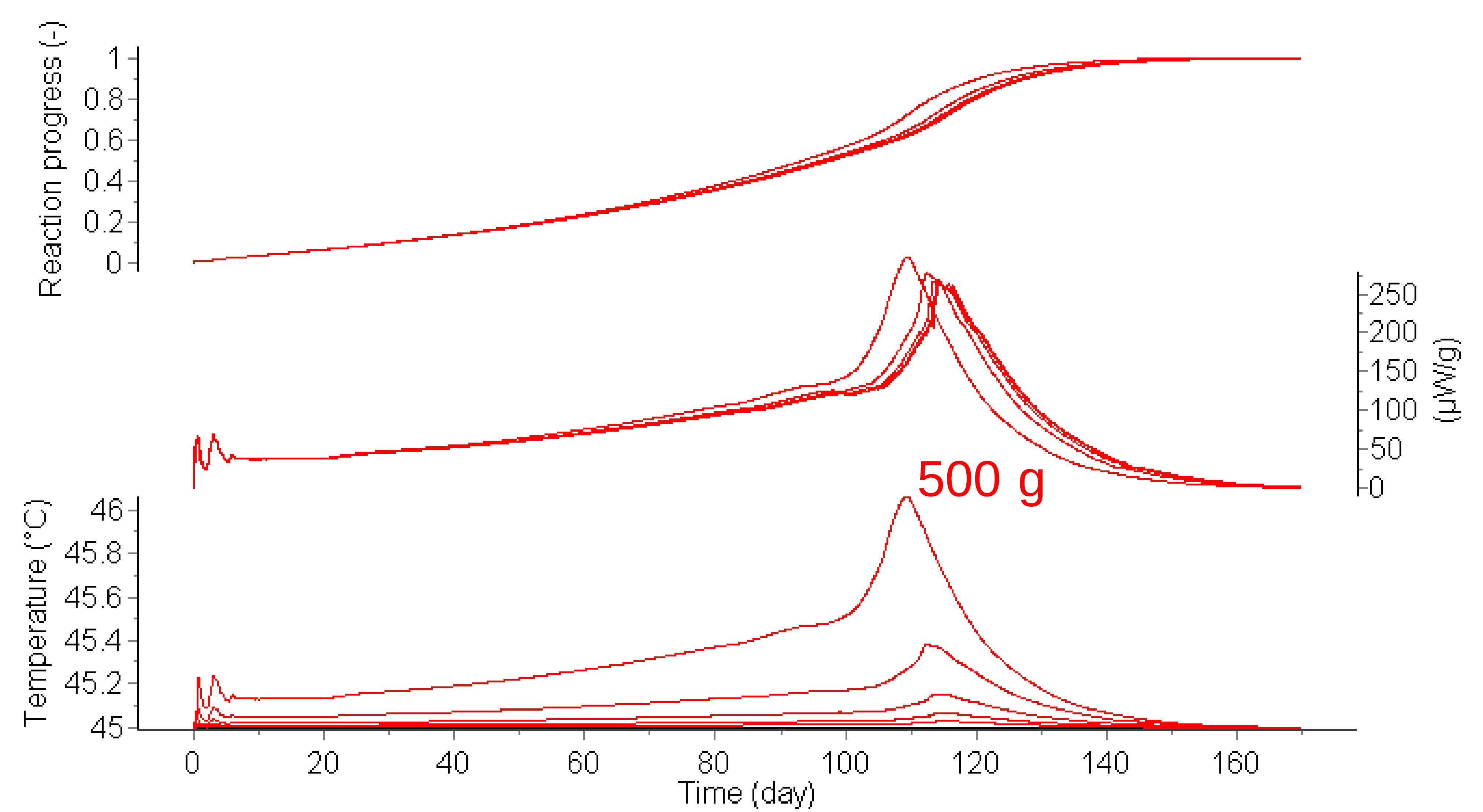

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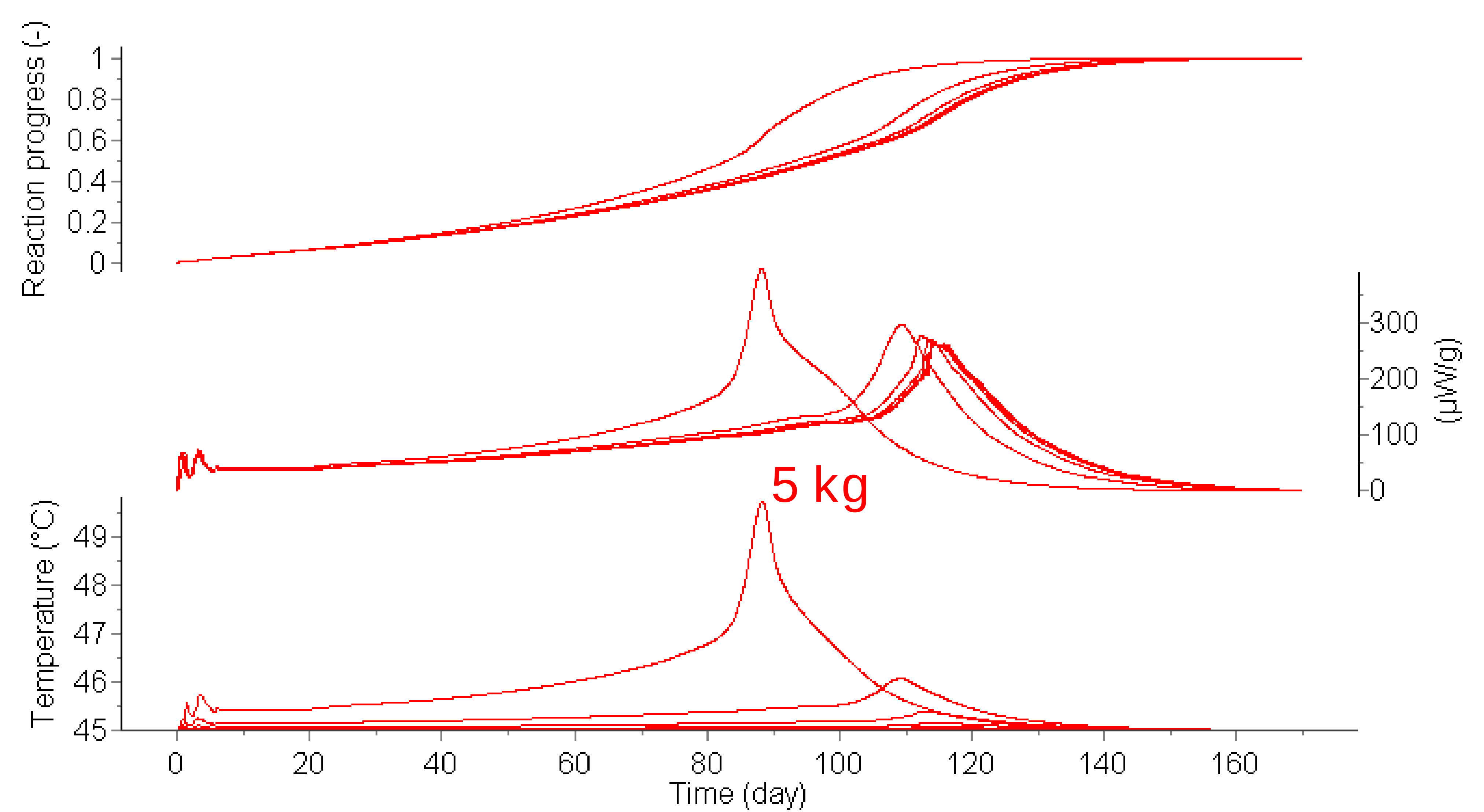

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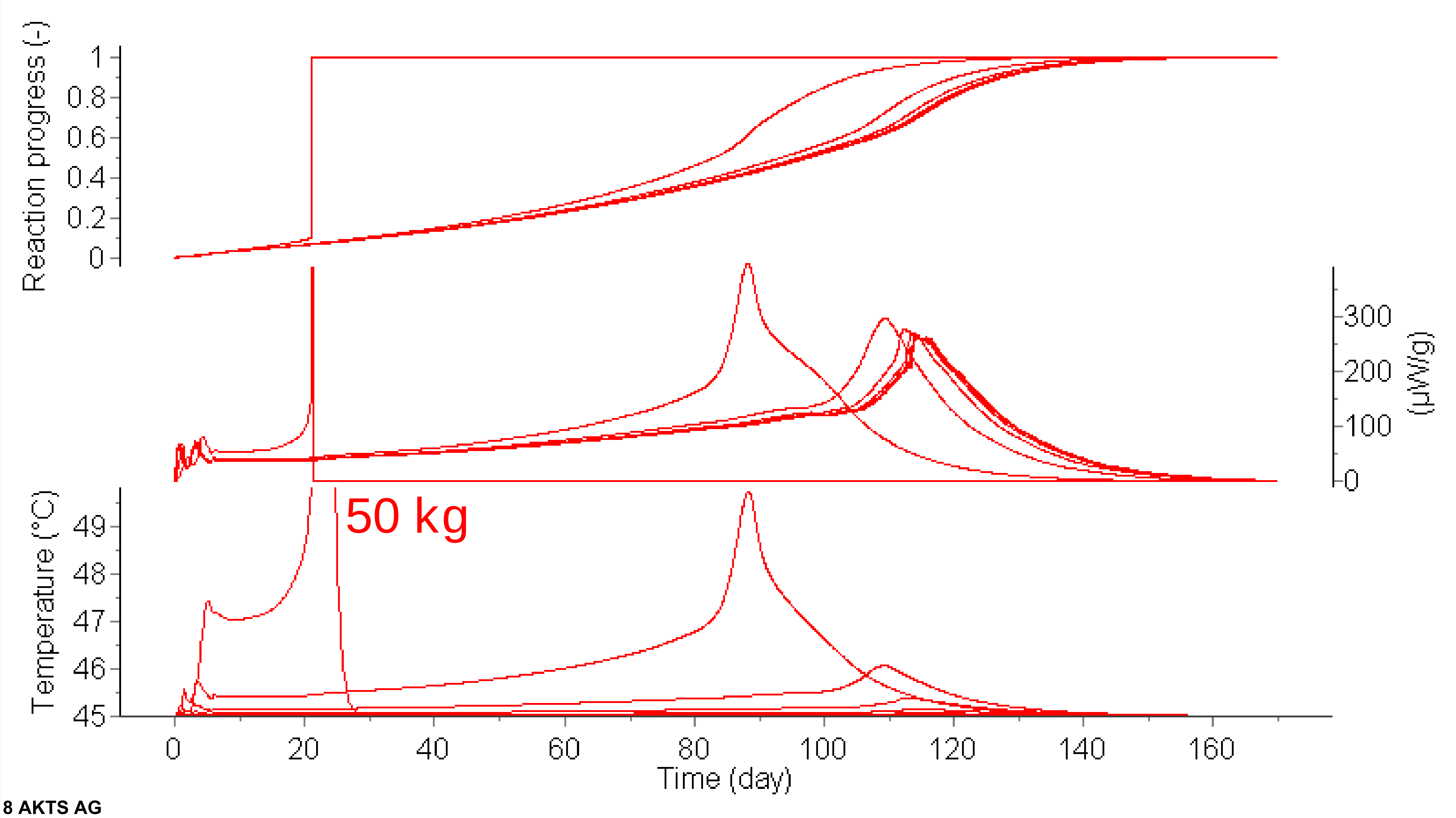

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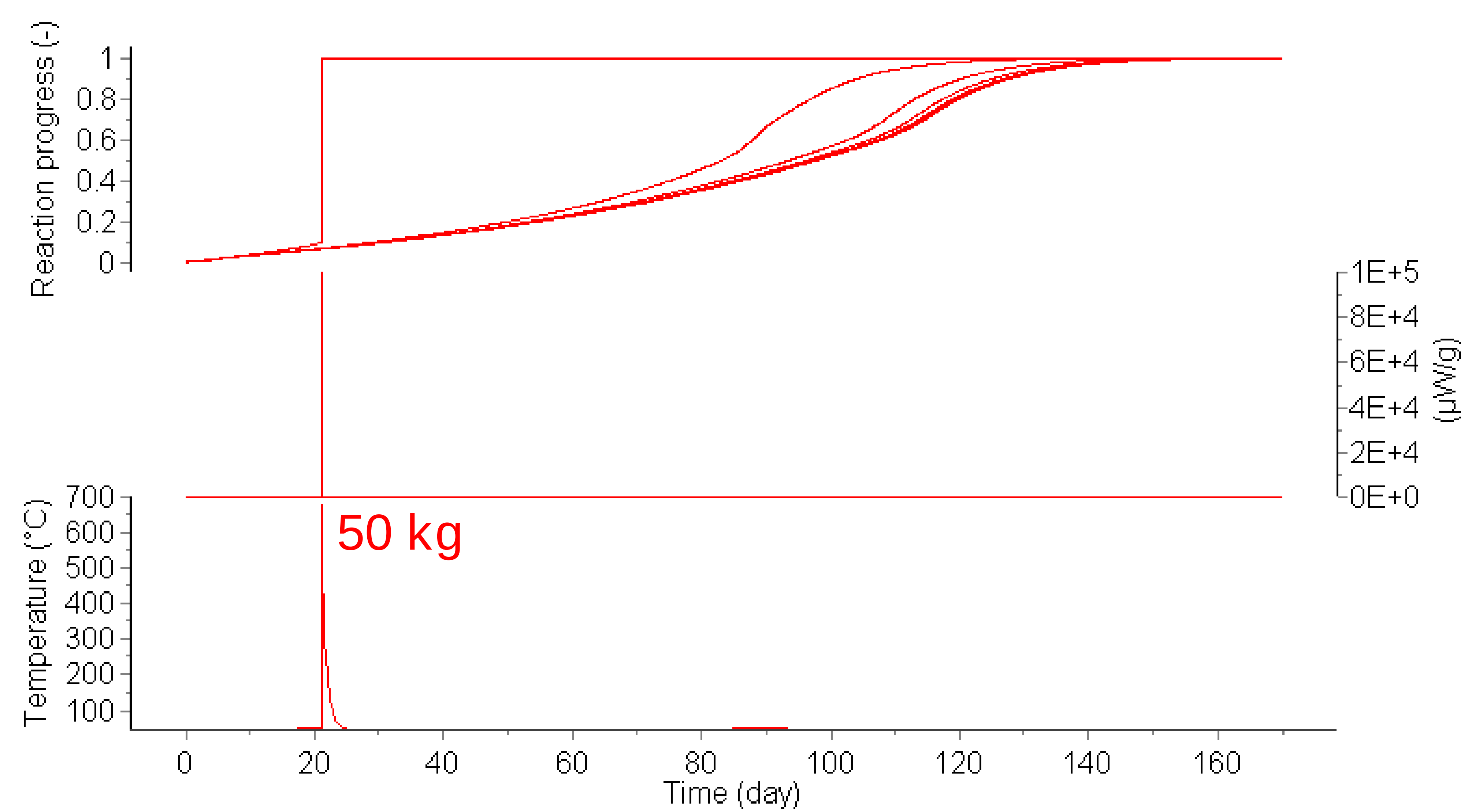

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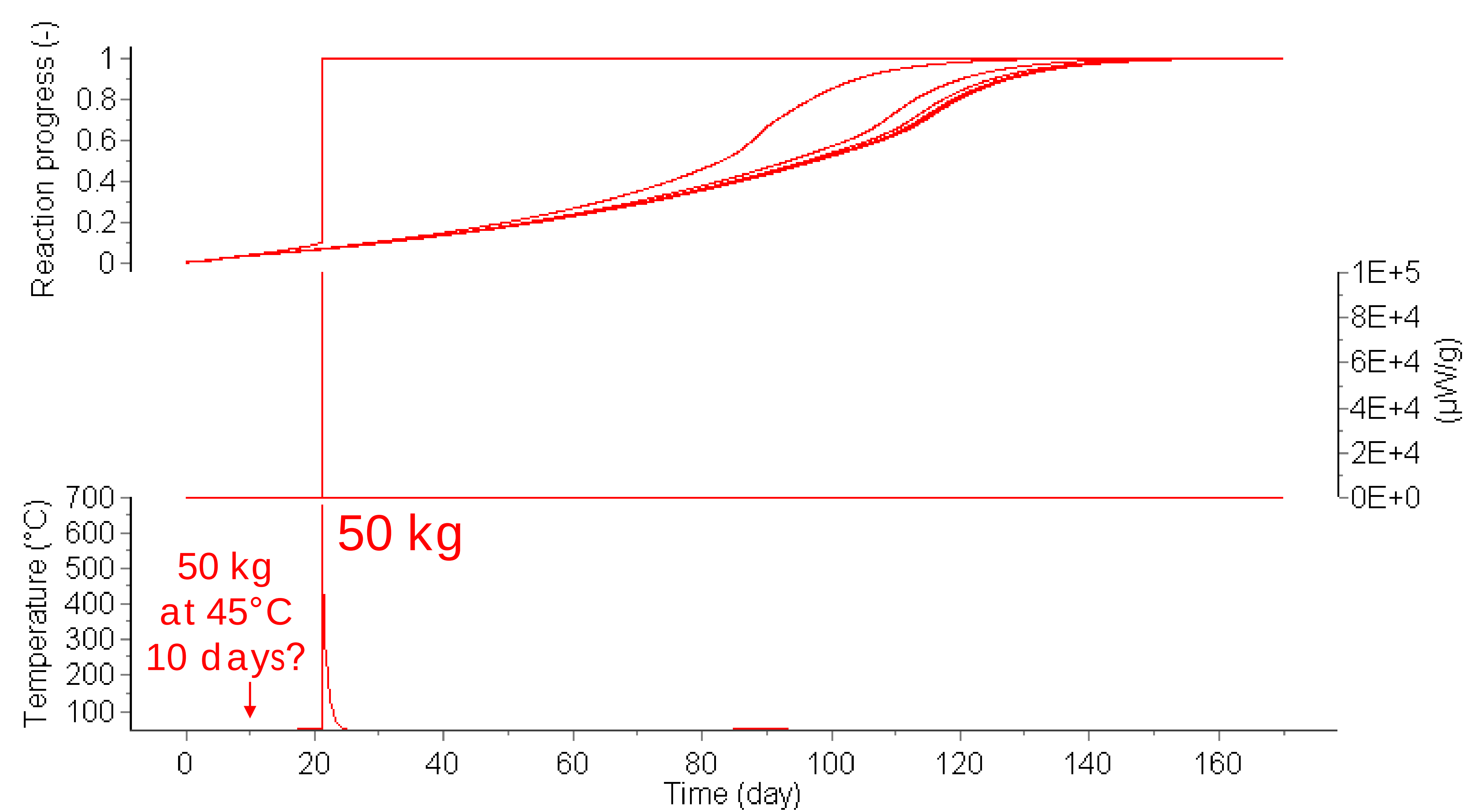


Are 50 kg of AIBN are stable
at surrounding temperature of 45°C
during a laps period of10 days?

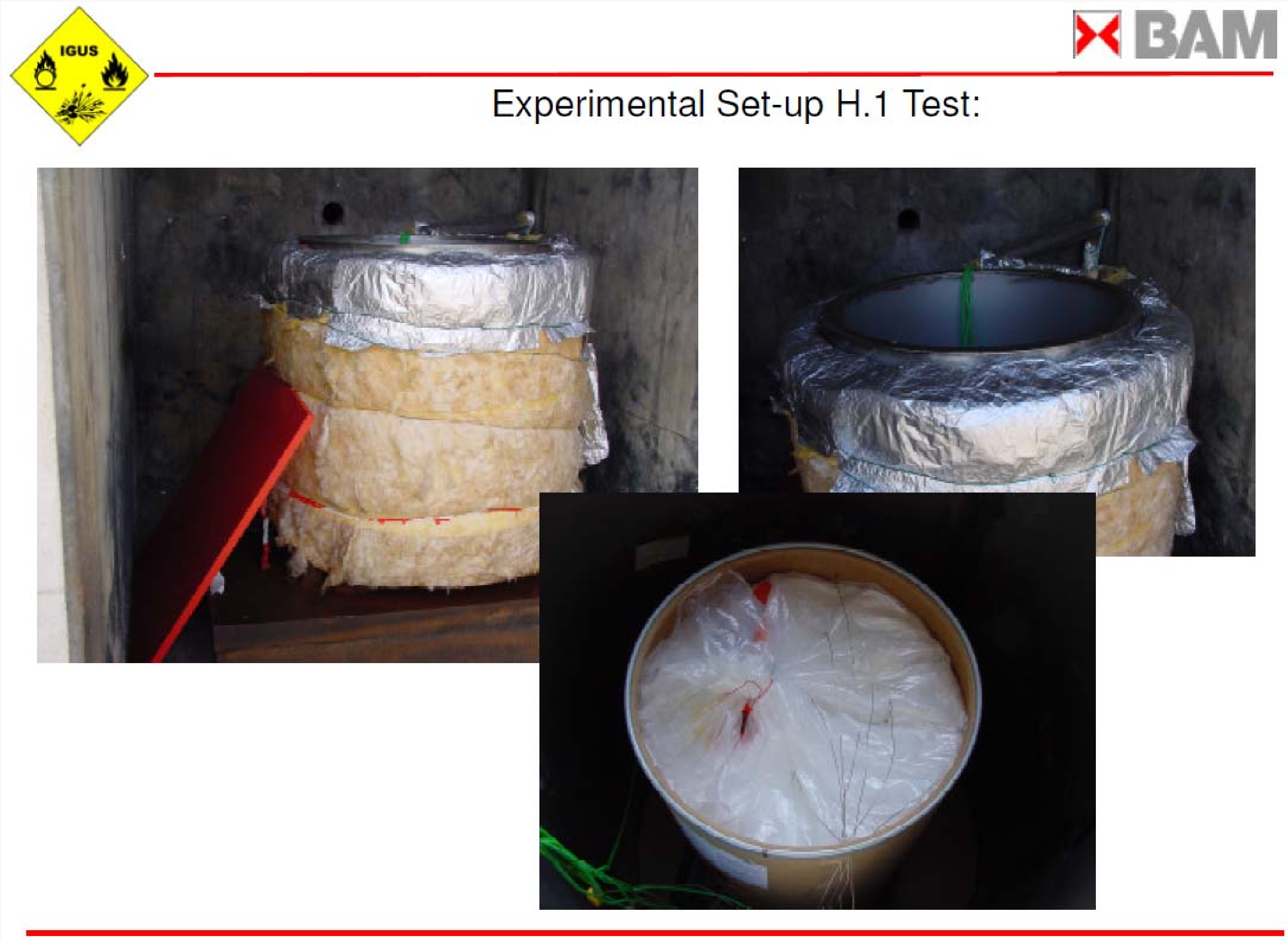
No ☐

Yes ☑

Experimental validation with a drum containing 50kg AIBN and exposed at 47°C during 10 days.

50 kg

47°C



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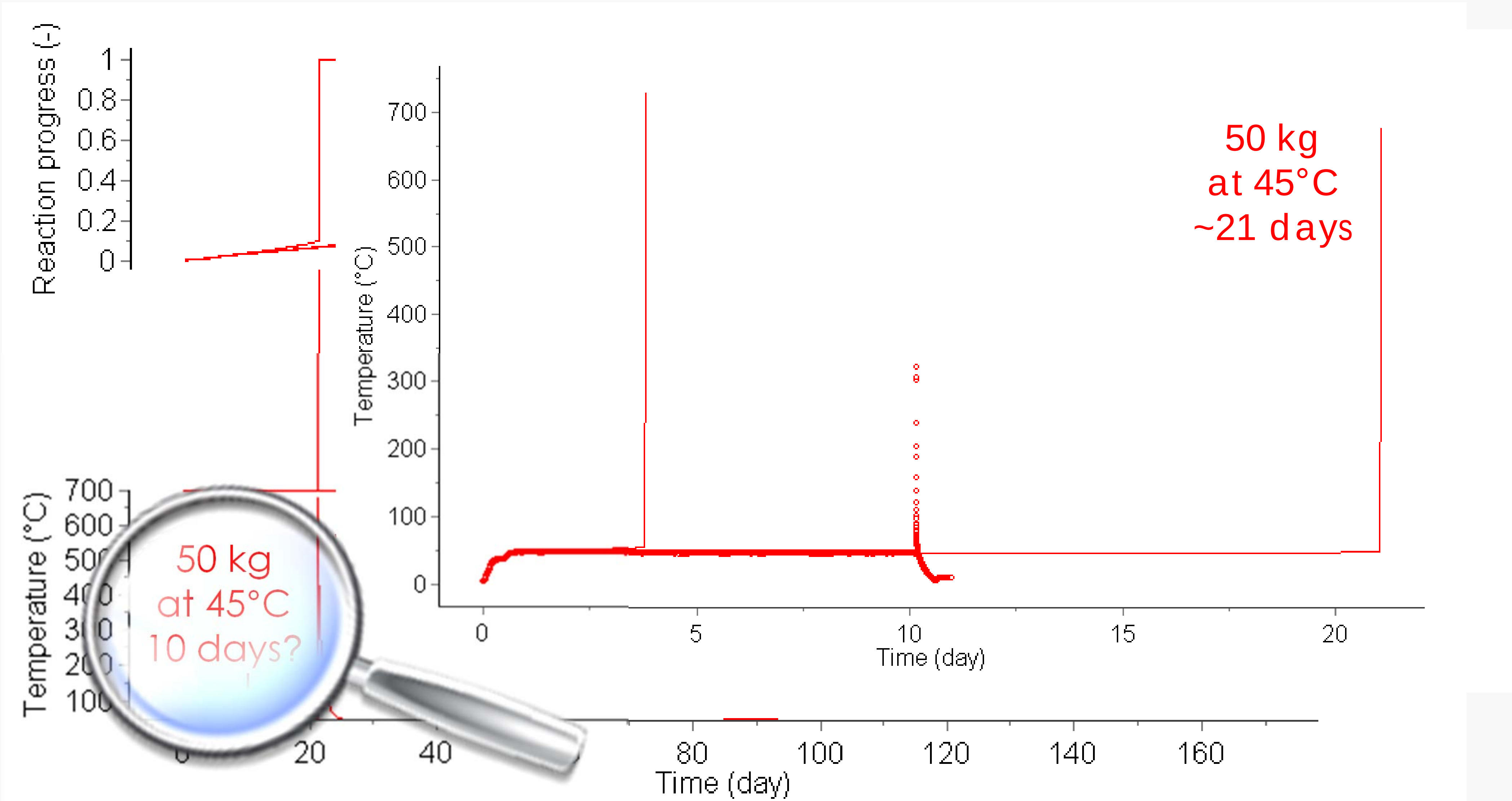

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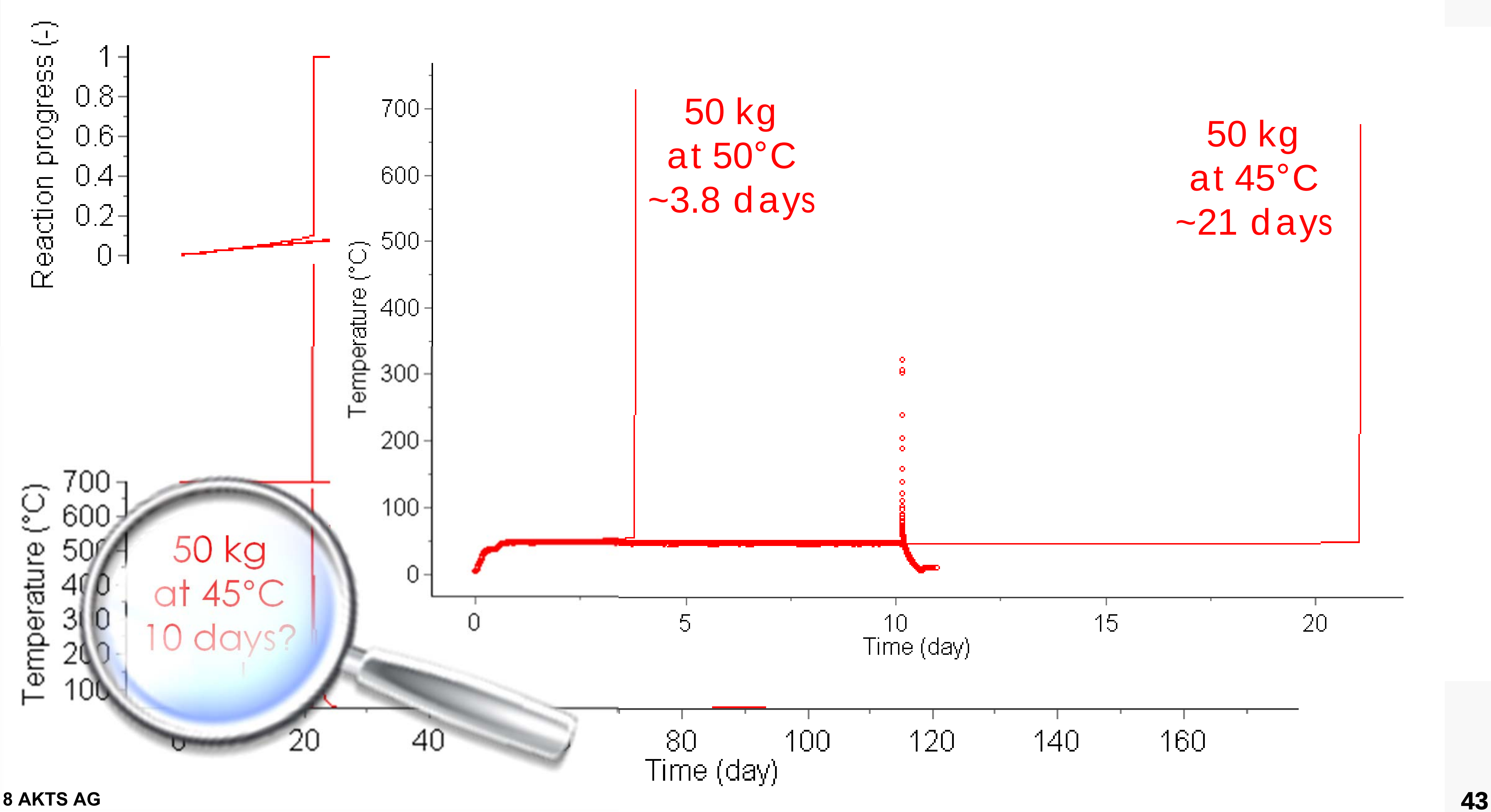

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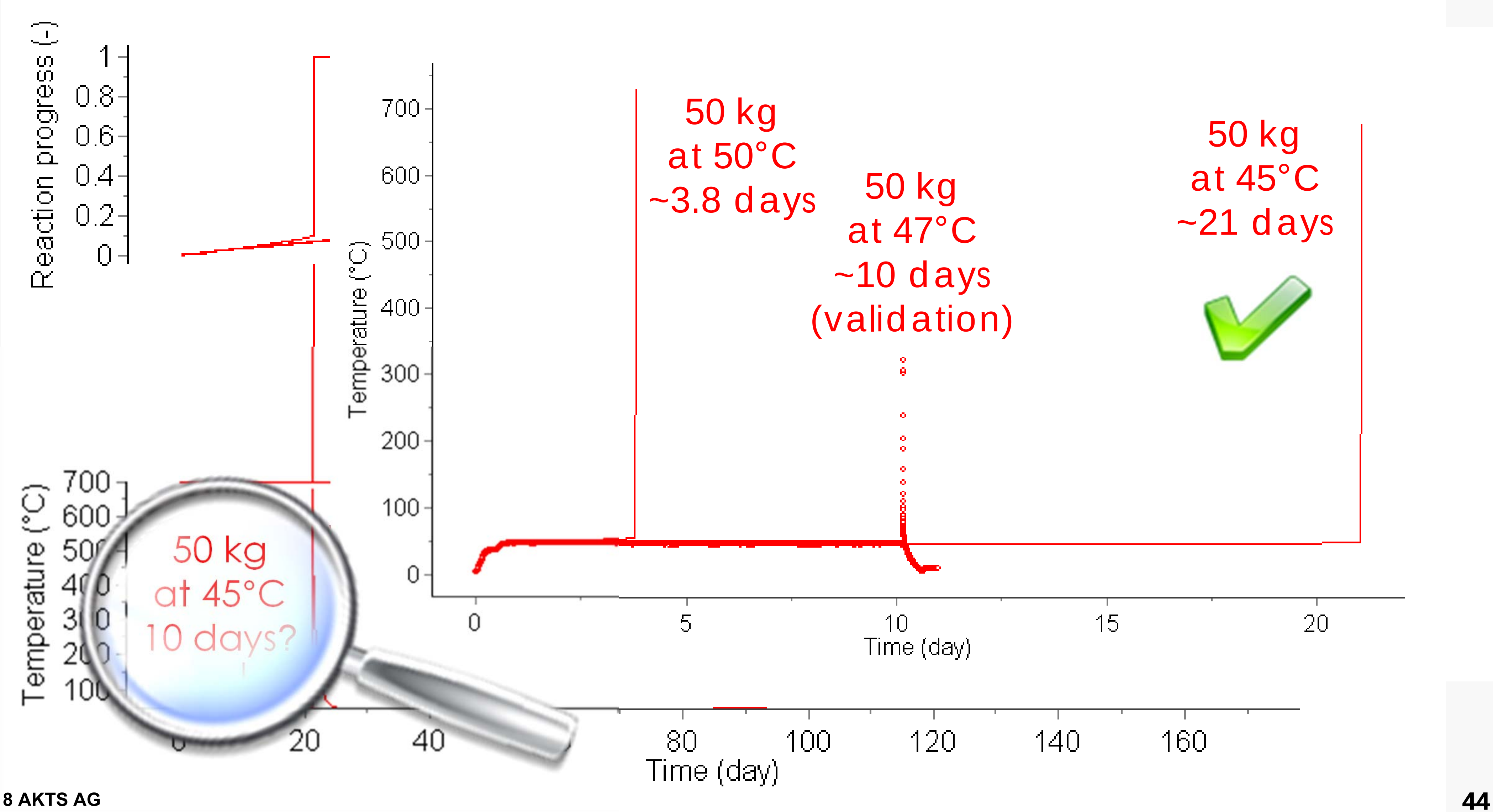

It possible to predict the thermal behavior during scale-up in which sample mass is increased by one million times.

For substances with polymorphic transition and melting before the exothermal event, ultra-sensitive heat flow measurements (HFC) may be applied.
HFC has a sensitivity with is about 1000 times better than in DSC and can be applied to collect the heat flow data of this phase which is stable at ambient temperatures during the long-term storage.

But summarizing, for successful scale-up, we need
-Kinetic description of the process
- Correct heat balance

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Thank you for your attention

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