Influence of the Chemical Composition of Propellants on Microcalorimetric Measurements

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Outline

- Introduction
- Aim
- Kinetic analysis
- Method
- Investigated propellants
- Results
  - HFC measurements
  - Kinetic parameters
  - Simulation
  - Simulation of a propellant using kinetic parameters from a similar propellant
- Conclusion

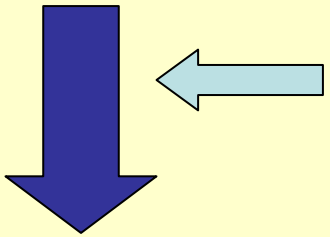
Introduction: Microcalorimetry

- Measurement of the beginning of the decomposition process with high precision

  (0%<α<5%)
- Use to assess the stability of propellant (Stanag 4582)

Aim

HFC measurements at minimum three different temperatures are time consuming



Kinetic parameters (Ea, A)

Is it reasonable to perform simulation for a propellant using kinetic parameters from a similar propellant ?

Kinetic analysis

Principle

Calculation based on the isoconversional principle of Friedman:

- Reaction rate at constant reaction progress α is only function of the temperature.

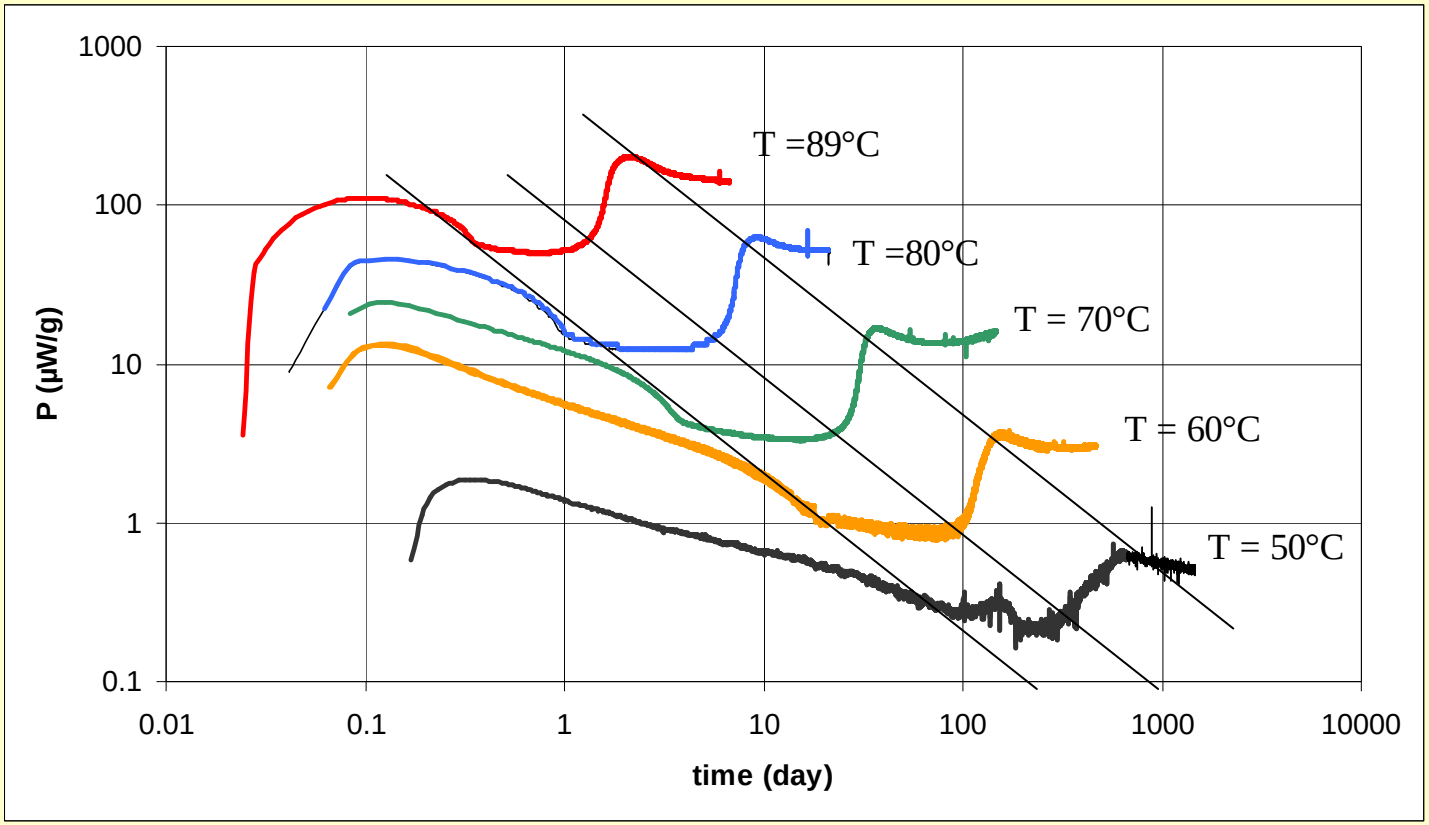
$$\ln\left(\frac{d\alpha}{dt_\alpha}\right) = \ln\{A_\alpha f(\alpha)\} - \frac{E_\alpha}{R}\frac{1}{T_\alpha}$$

- Calculation performed with a software from AKTS

Kinetic analysis

Principle

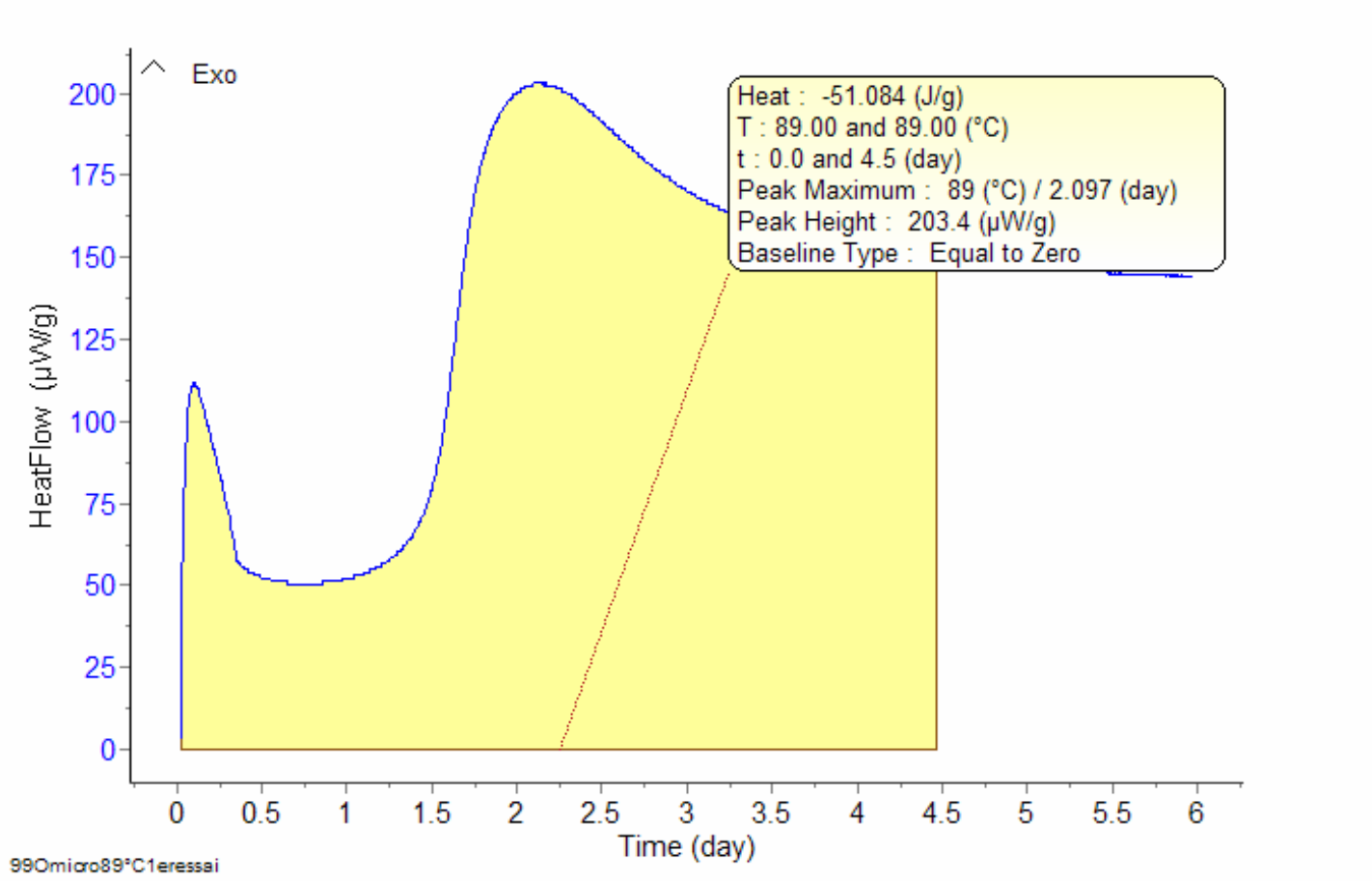
Measurement at at least three different temperatures



Kinetic analysis

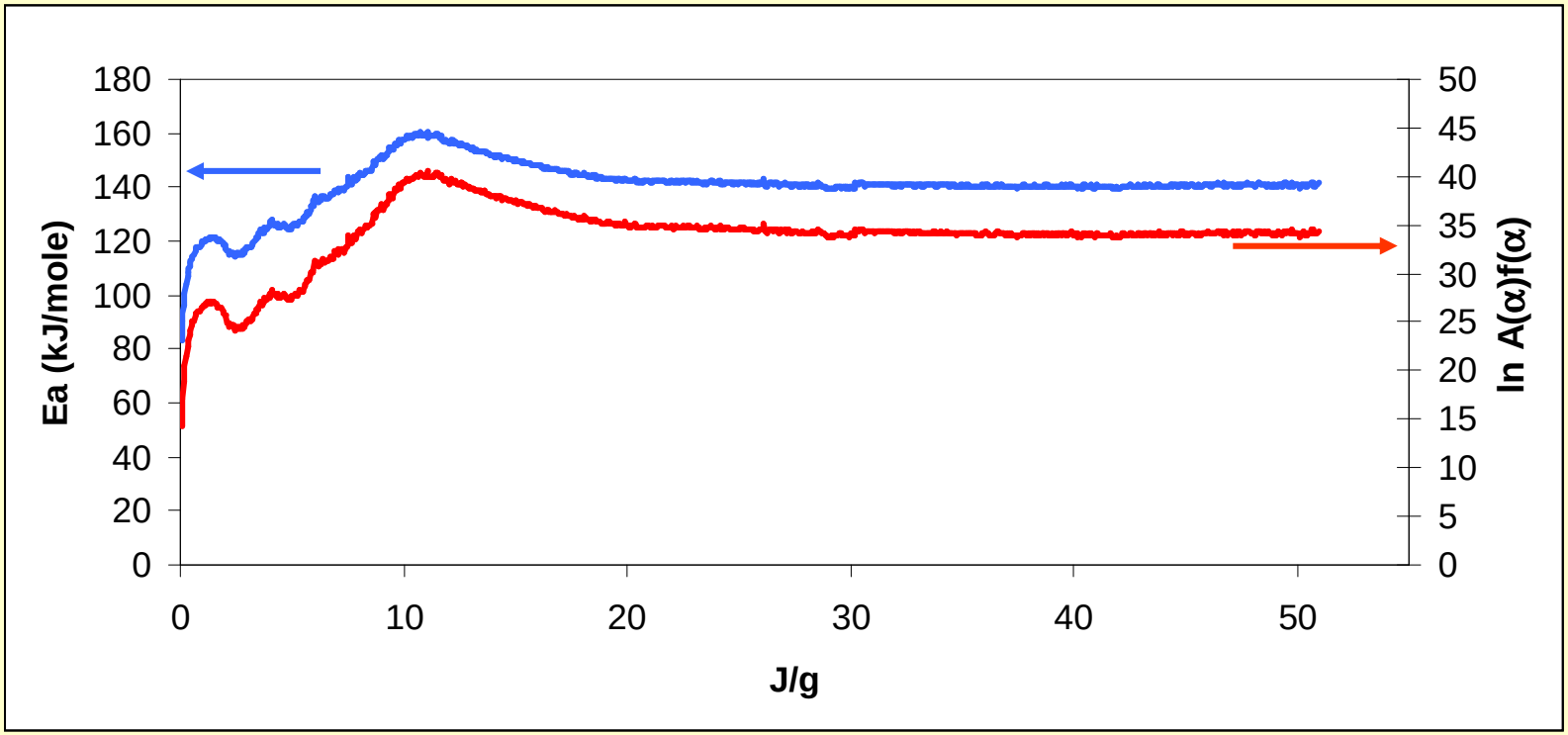
Principle

All the curves must be integrated to the same energy values



Kinetic analysis

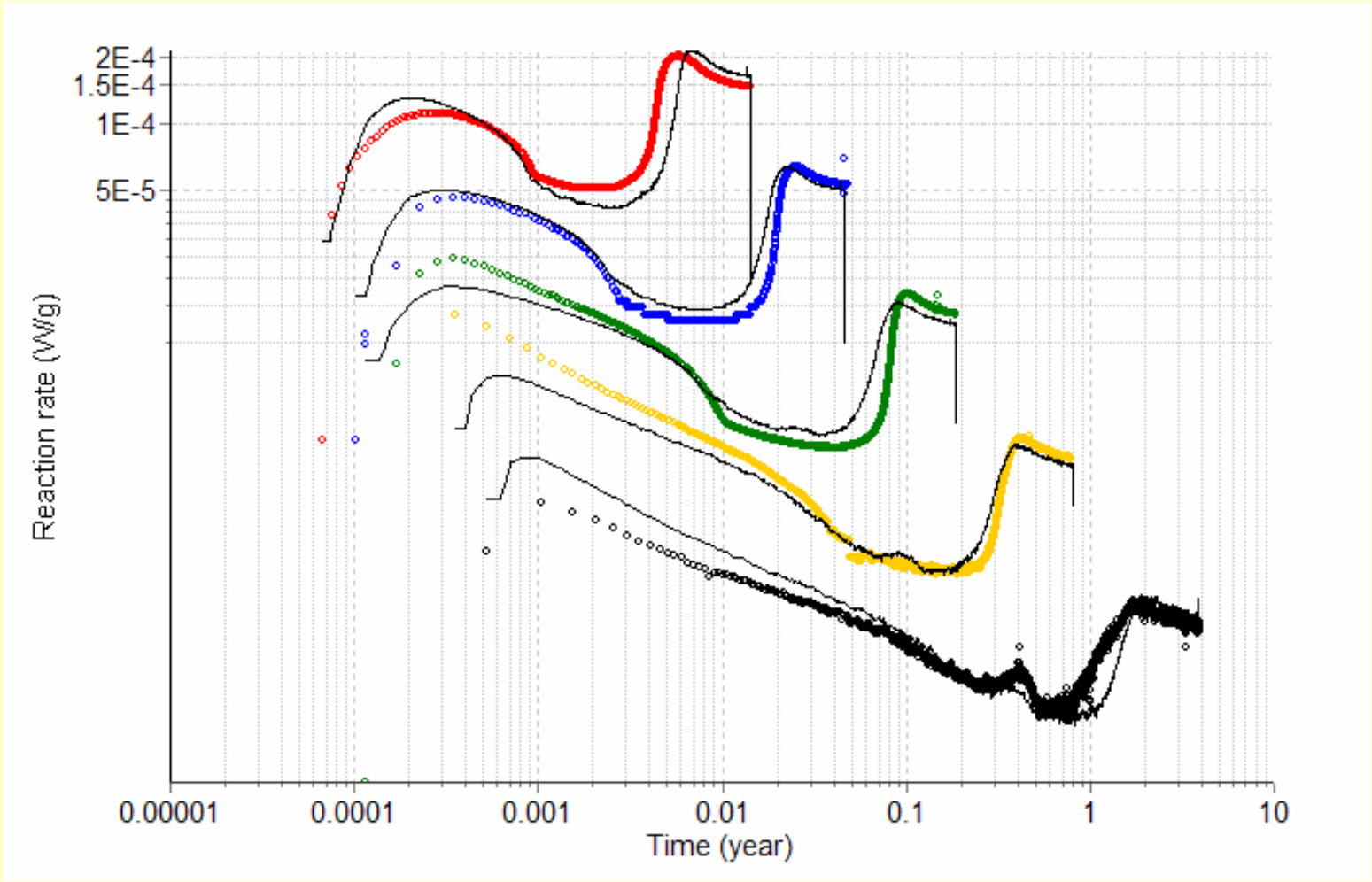
Calculation of the kinetic factors



⇒ Possibility to simulate the measured curves and to do prediction

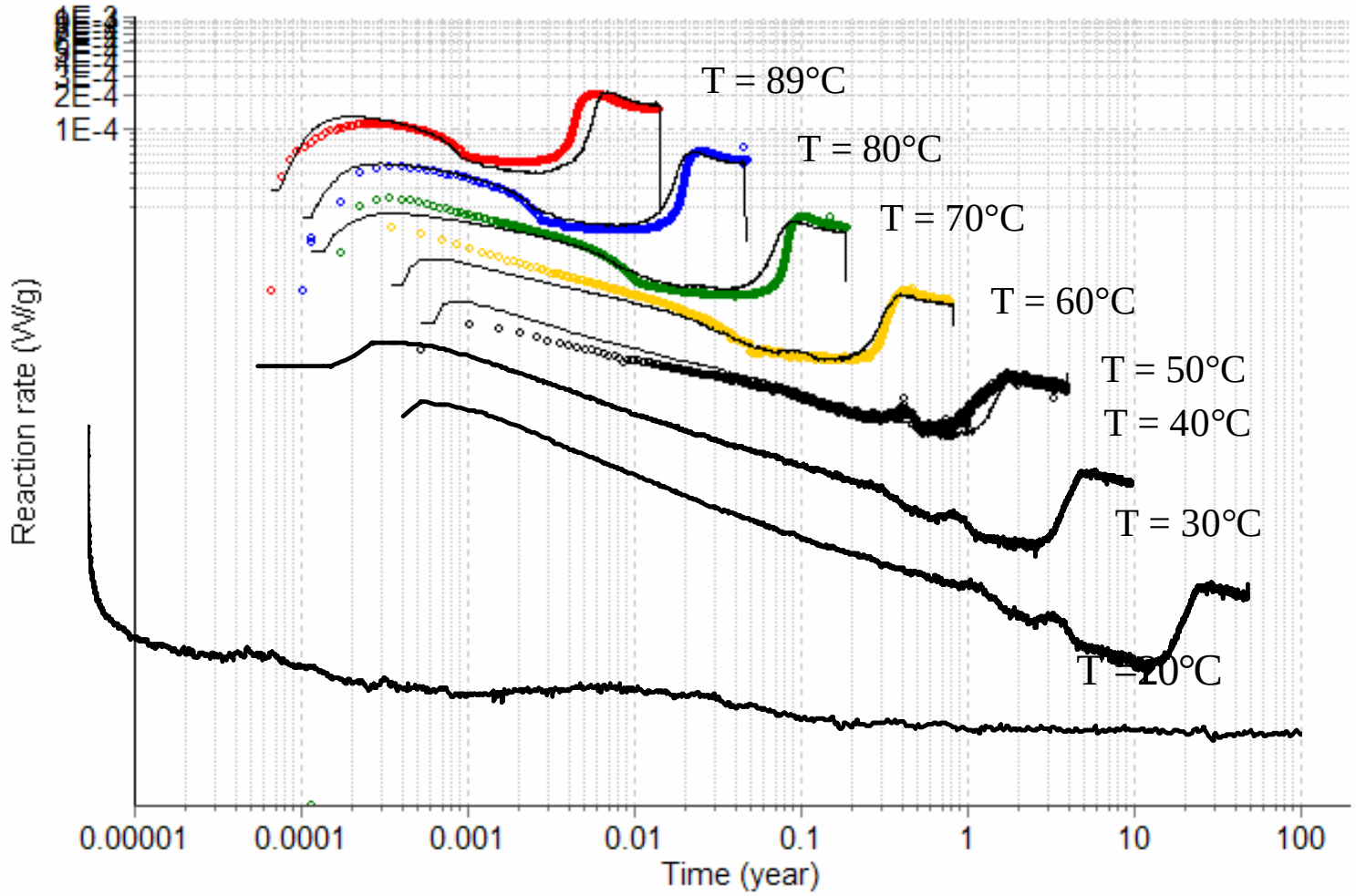
Kinetic analysis

Simulation



Kinetic analysis

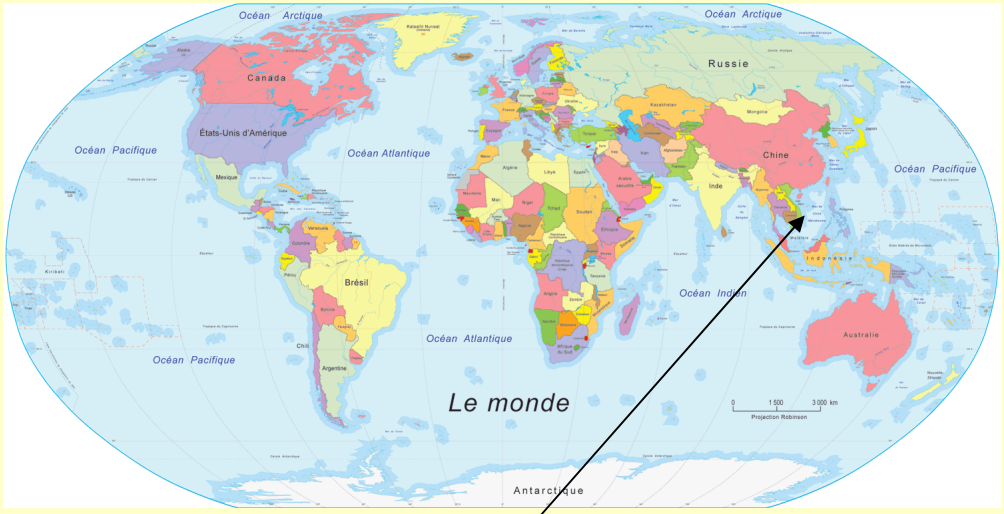
Predictions



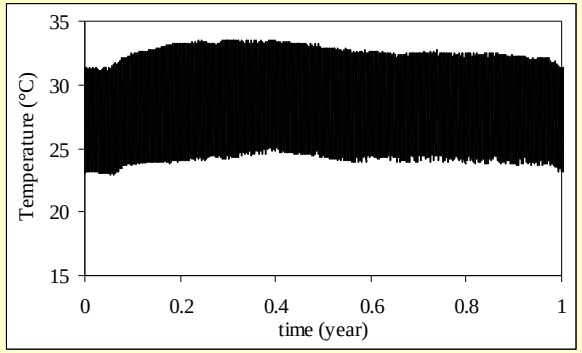
Kinetic analysis

Predictions

What happens if a propellant stays 10 years in Malaysia ?



?

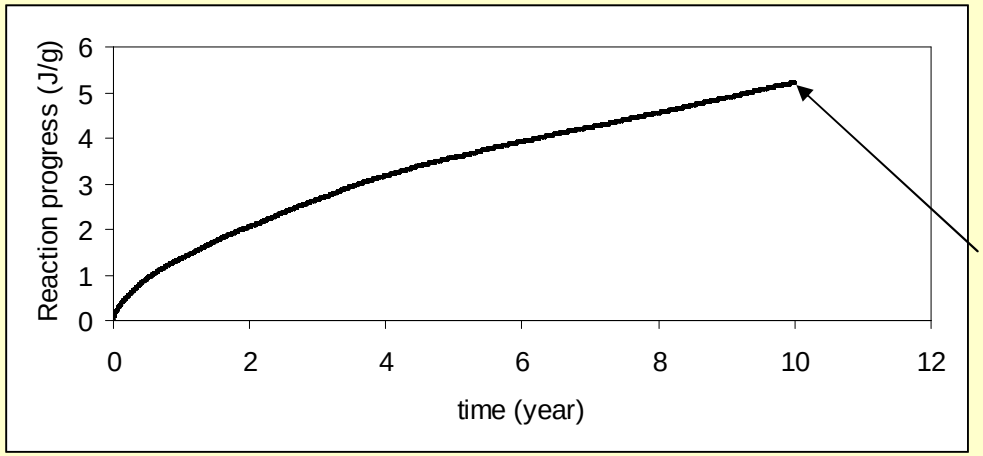


Use of a standard weather temperature profile

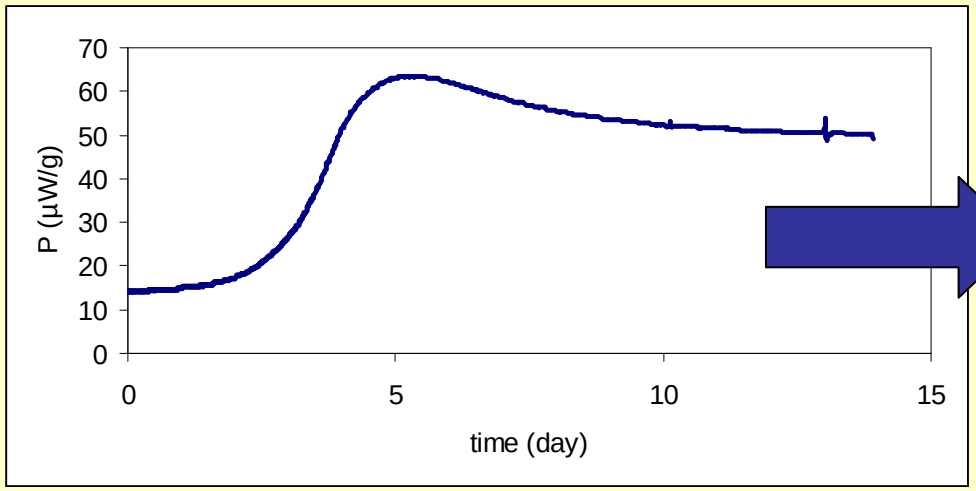
Kinetic analysis

Predictions

10 years in Malaysia



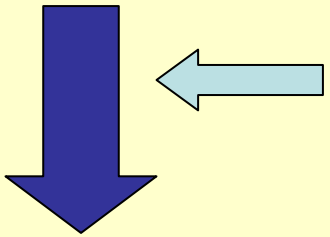
Simulation of a microcalorimetric experiment at 80°C



Possibility to compare experimental and simulated results

Aim

HFC measurements at minimum three different temperatures are time consuming



Kinetic parameters (Ea, A)

Is it reasonable to perform simulation for a propellant using kinetic parameters from a similar propellant ?

Method

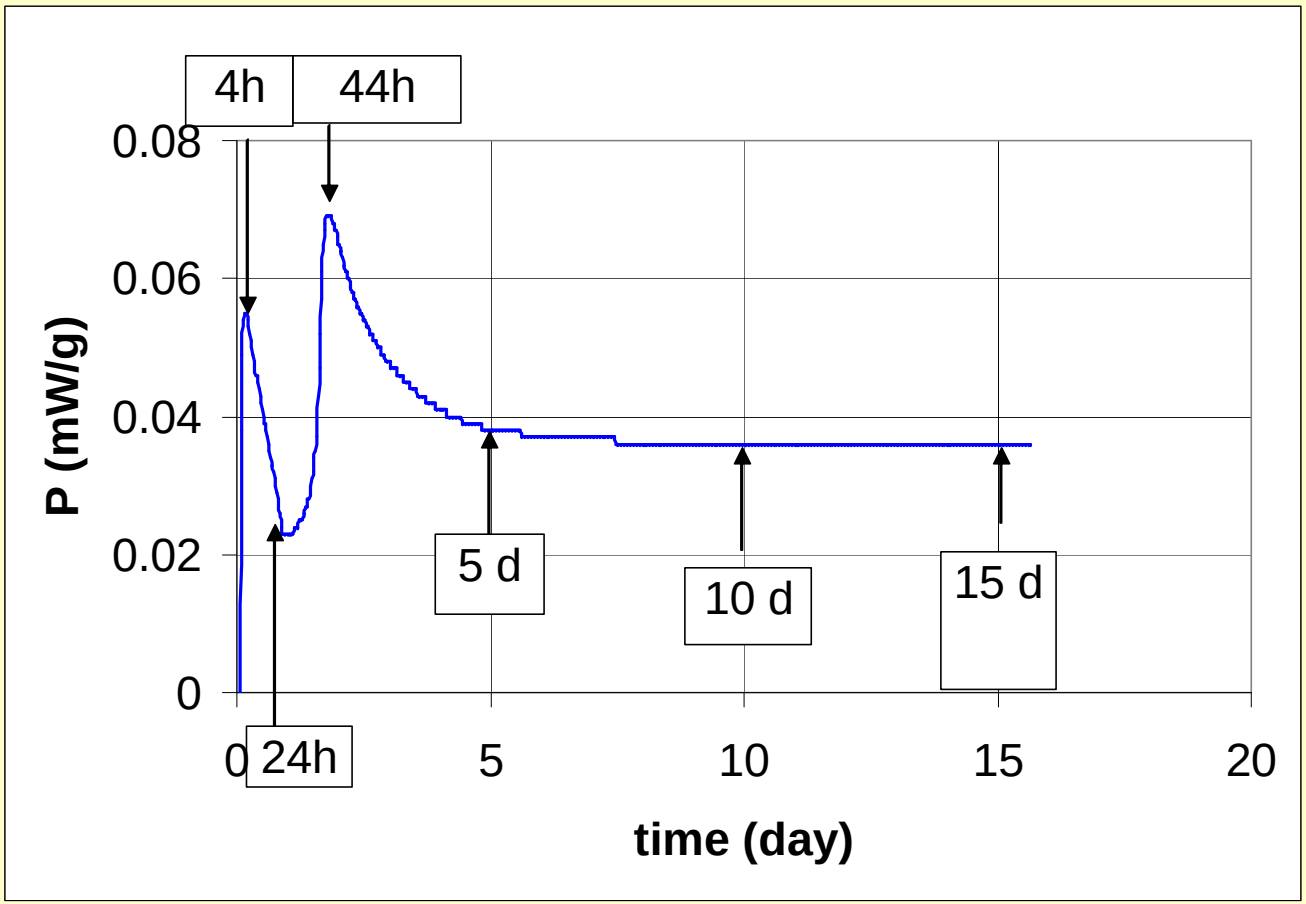
- Determination of kinetic parameters from propellants having different contents in nitroglycerin
- Simulation of a propellant aged at different conditions using parameters from a similar propellant

Investigated propellants

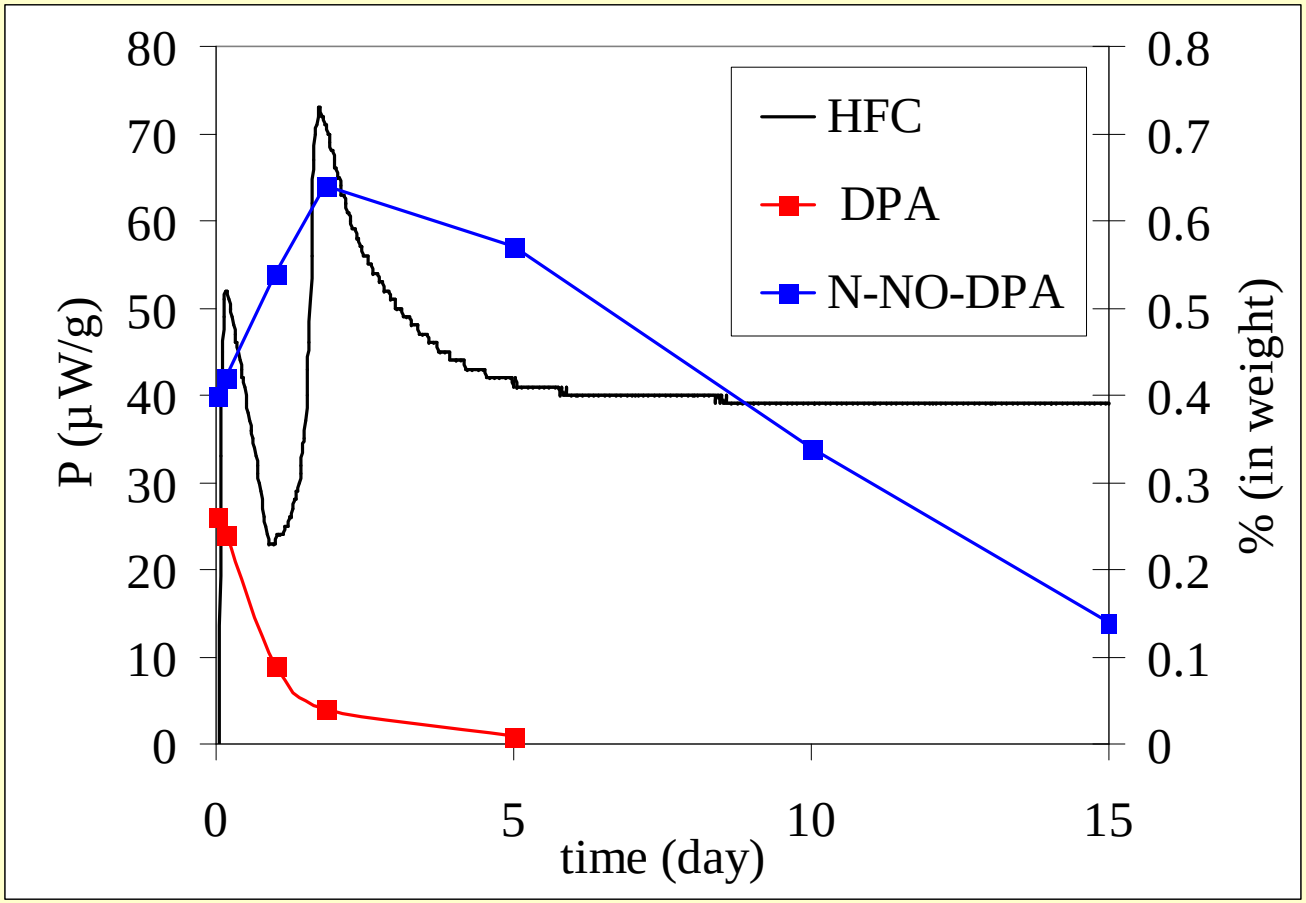
	%Ngl	%DPA	%N-NO-DPA*	%DBP**	Shape
Propellant A	11.1	0.65	0.54	0	spherical
Propellant B	11.0	0.64	0.54	0	flattened
Propellant C	10.5	0.60	0.51	4.6	flattened
Propellant D	10.6	0.65	0.41	4.8	flattened
Propellant E	19.2	0.49	0.46	5.1	flattened
Propellant F	25.5	0.45	0.49	0	flattened
Propellant G	41.6	0.25	0.59	0	flattened

Result: HFC Measurement

For propellant containing DPA: relation between signal shape and stabilizer concentration

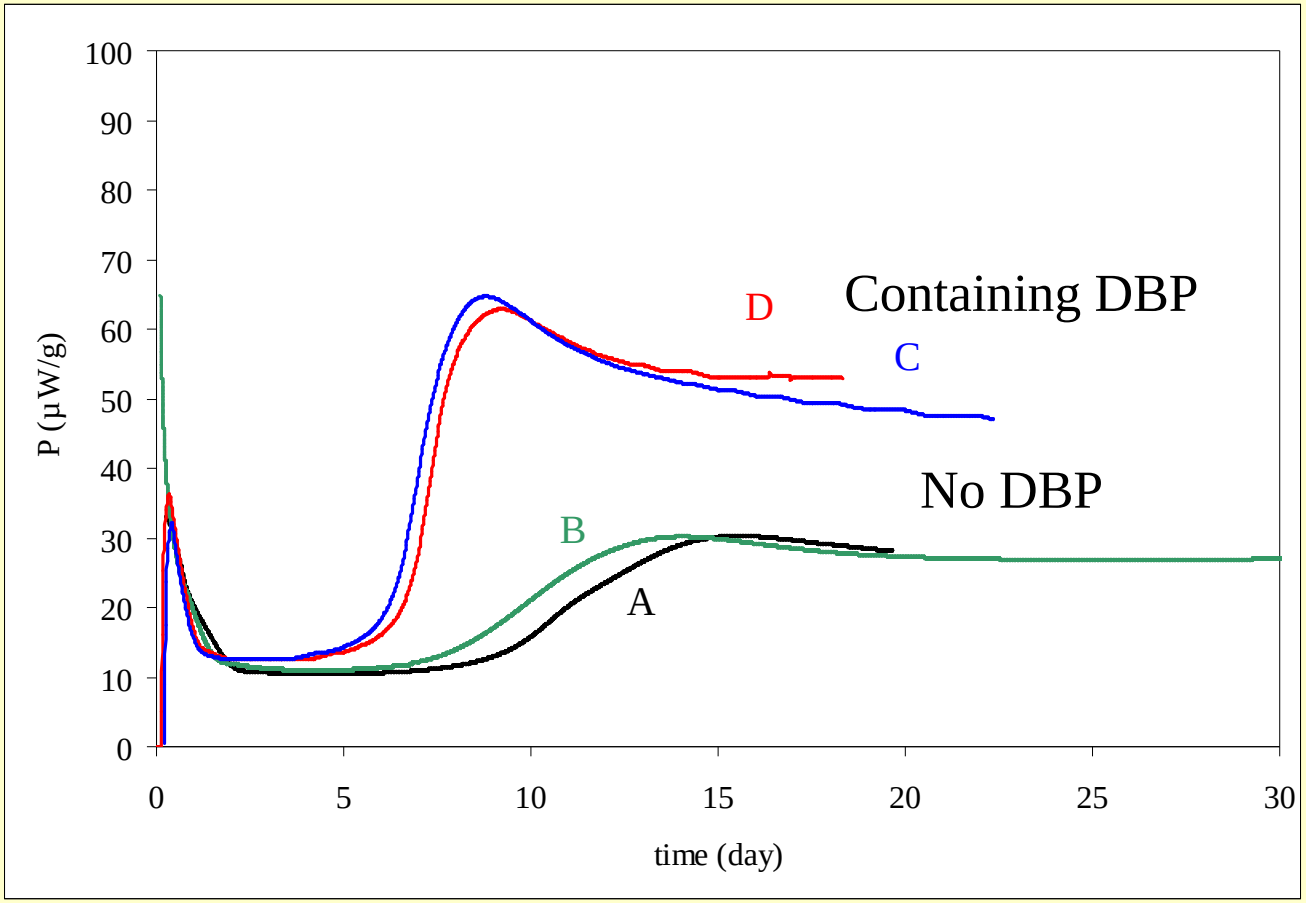


Result: HFC Measurement



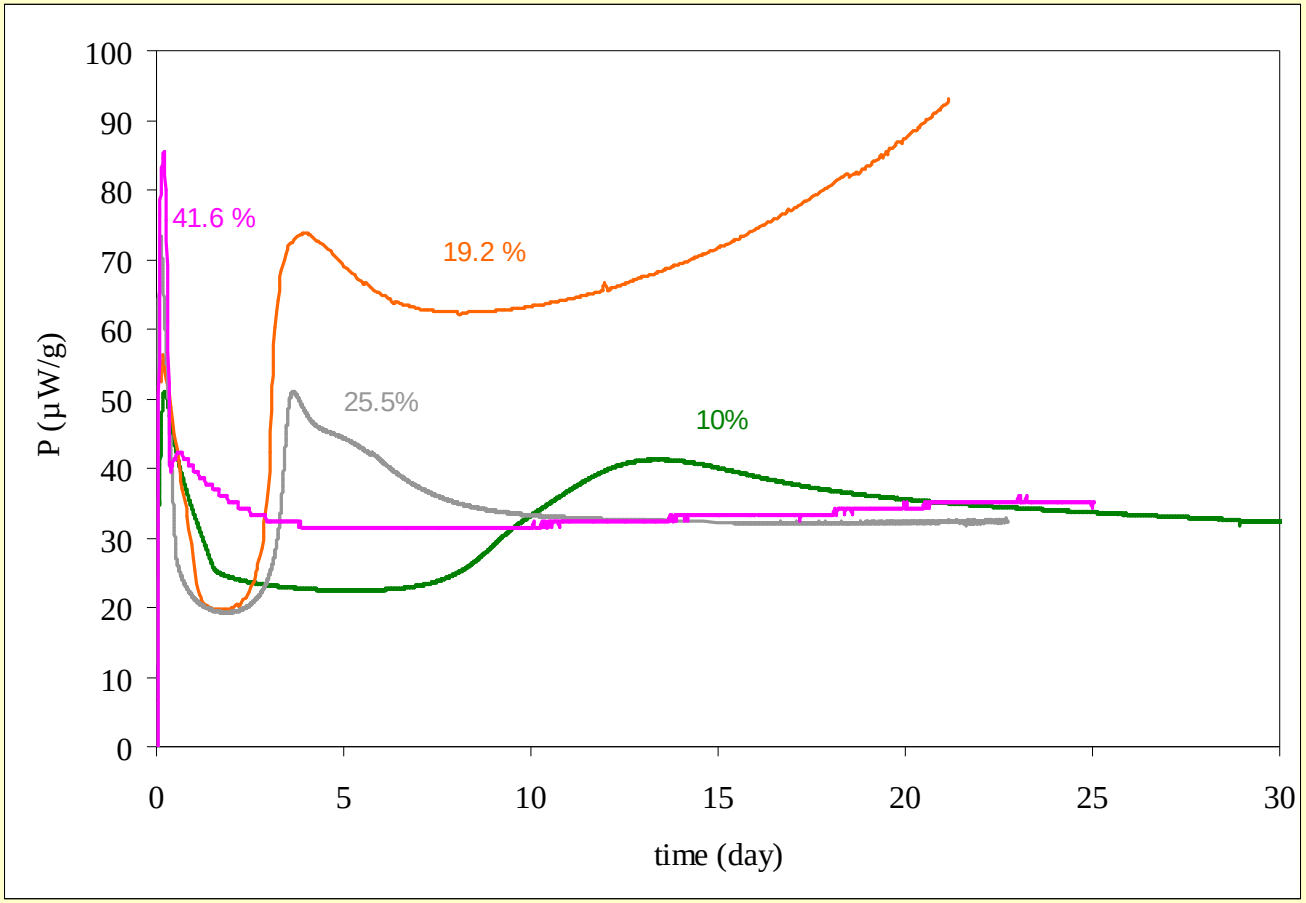
Result: HFC Measurement

Propellant containing about 10% of nitroglycerin

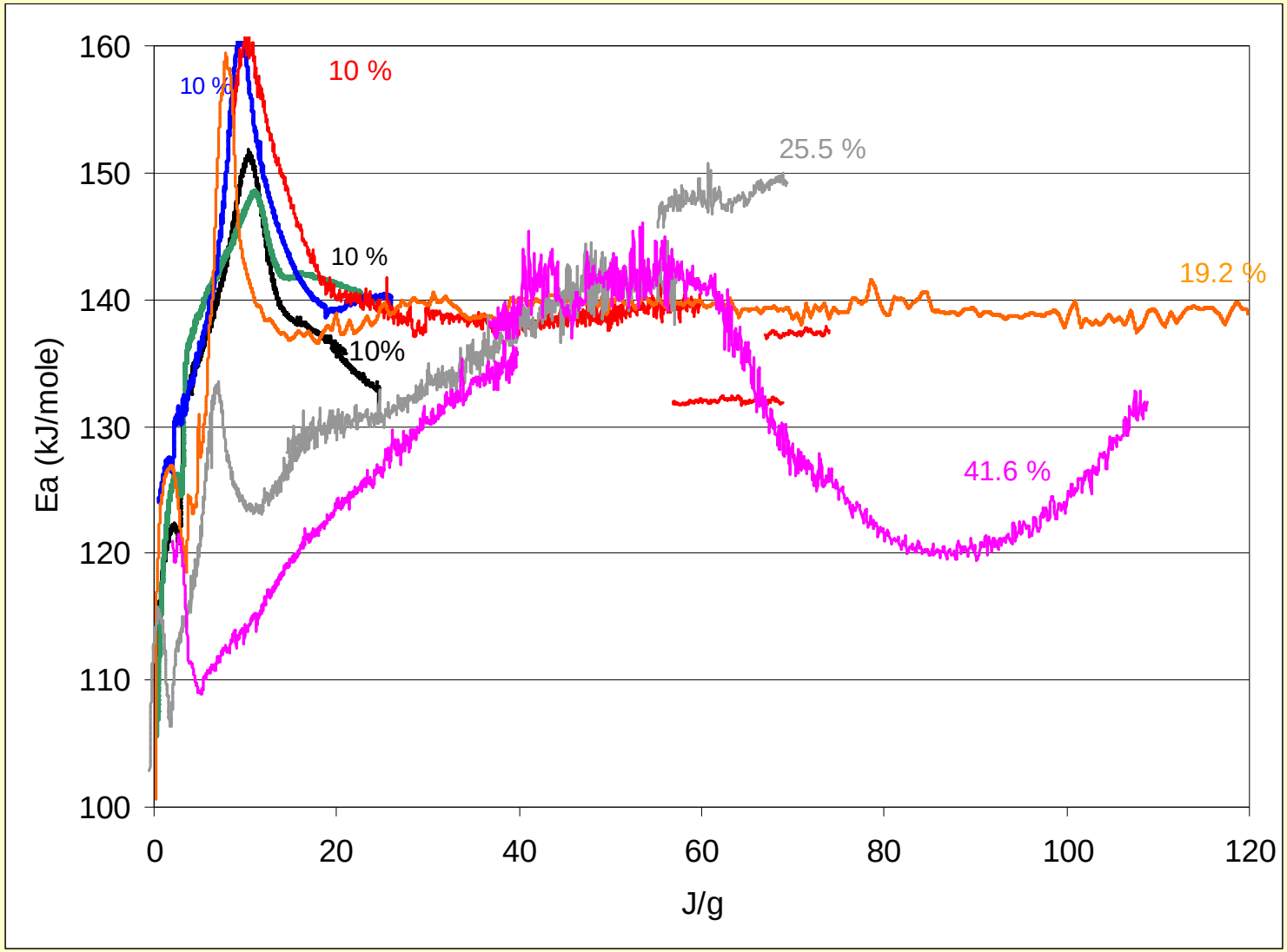


Result: HFC Measurement

Propellant containing different contents in nitroglycerin

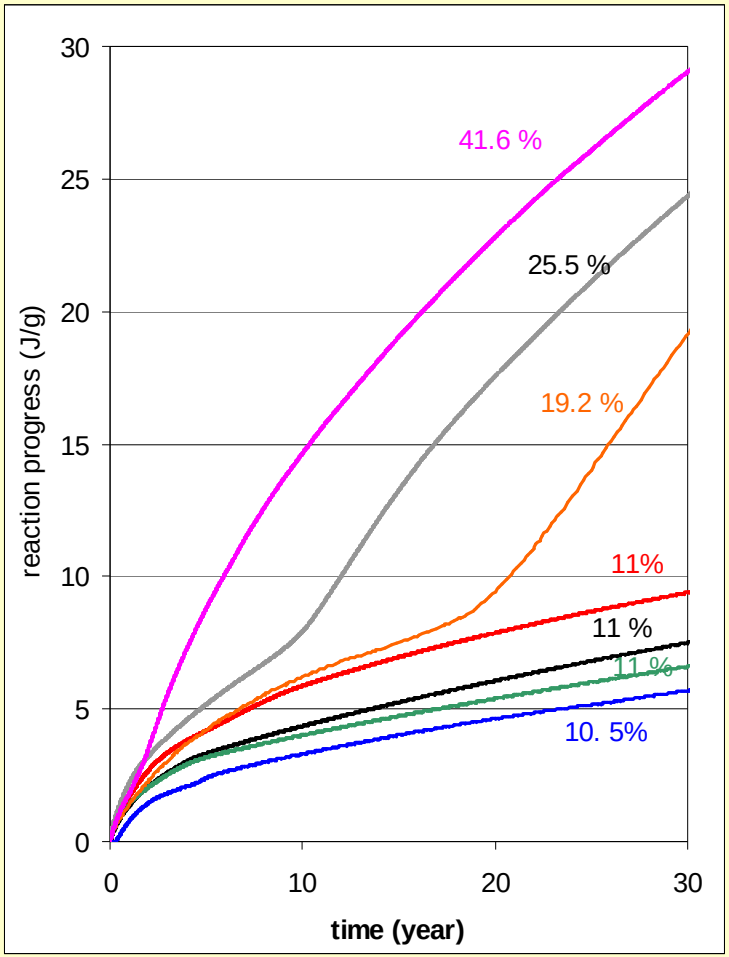


Result: Kinetic parameters

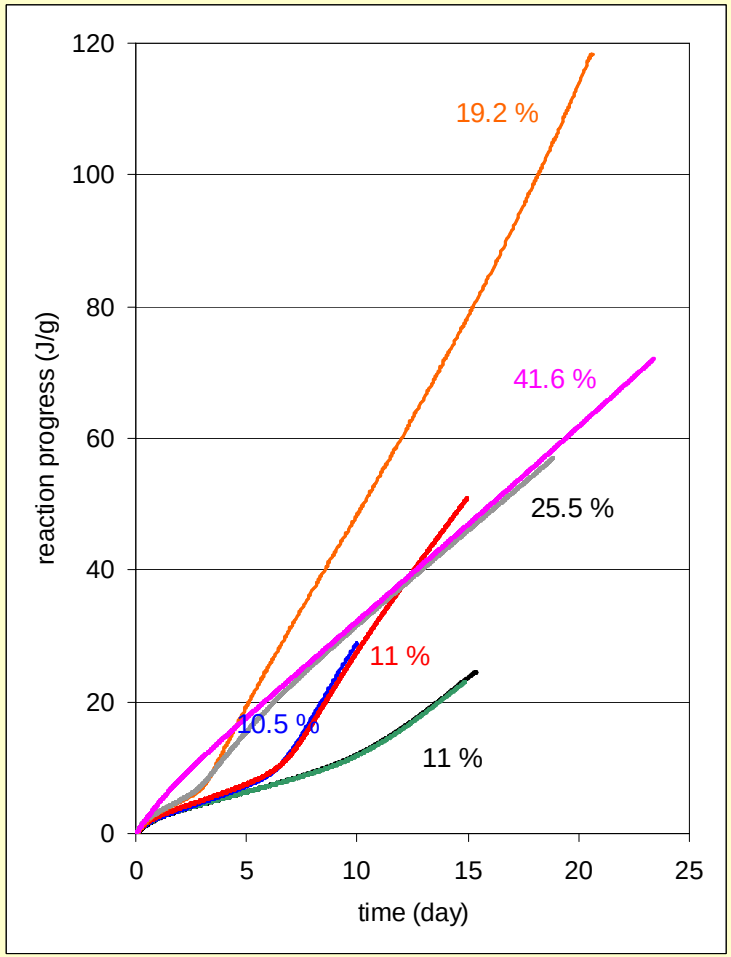


Result: Simulation

30 °C



80 °C



Result: Simulation of a propellant using kinetic parameters from a similar propellant

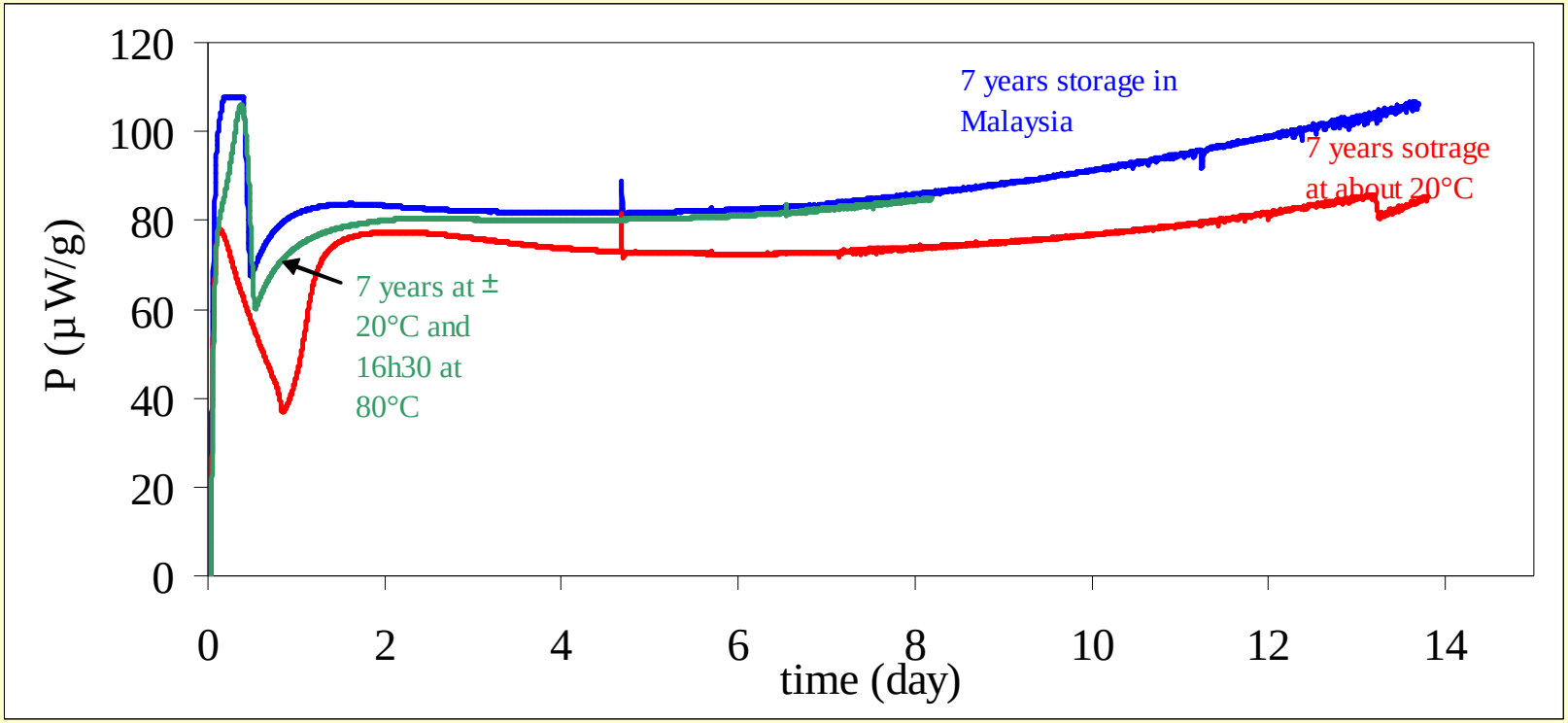
Propellant aged at different conditions

Limitation: no measurement of this propellant before ageing

Ageing time	%Ngl	%DPA	%N-NO-DPA	%DBP
t_0	19.0	0.32	0.60	5.9
t_0 + 7 years at 22°C ± 2°C	19.0	0.08	0.64	5.9
t_0 + 7 years in Malaysia	19.0	0.1	0.68	5.9
t_0 + 19 years at 22°C ± 2°C	19.0	0.10	0.52	5.9
t_o + 7 years at 22°C ± 2°C + 16h30 at 80°C	19.0	0.08	0.64	5.9

Result: Simulation of a propellant using kinetic parameters from a similar propellant

Available results



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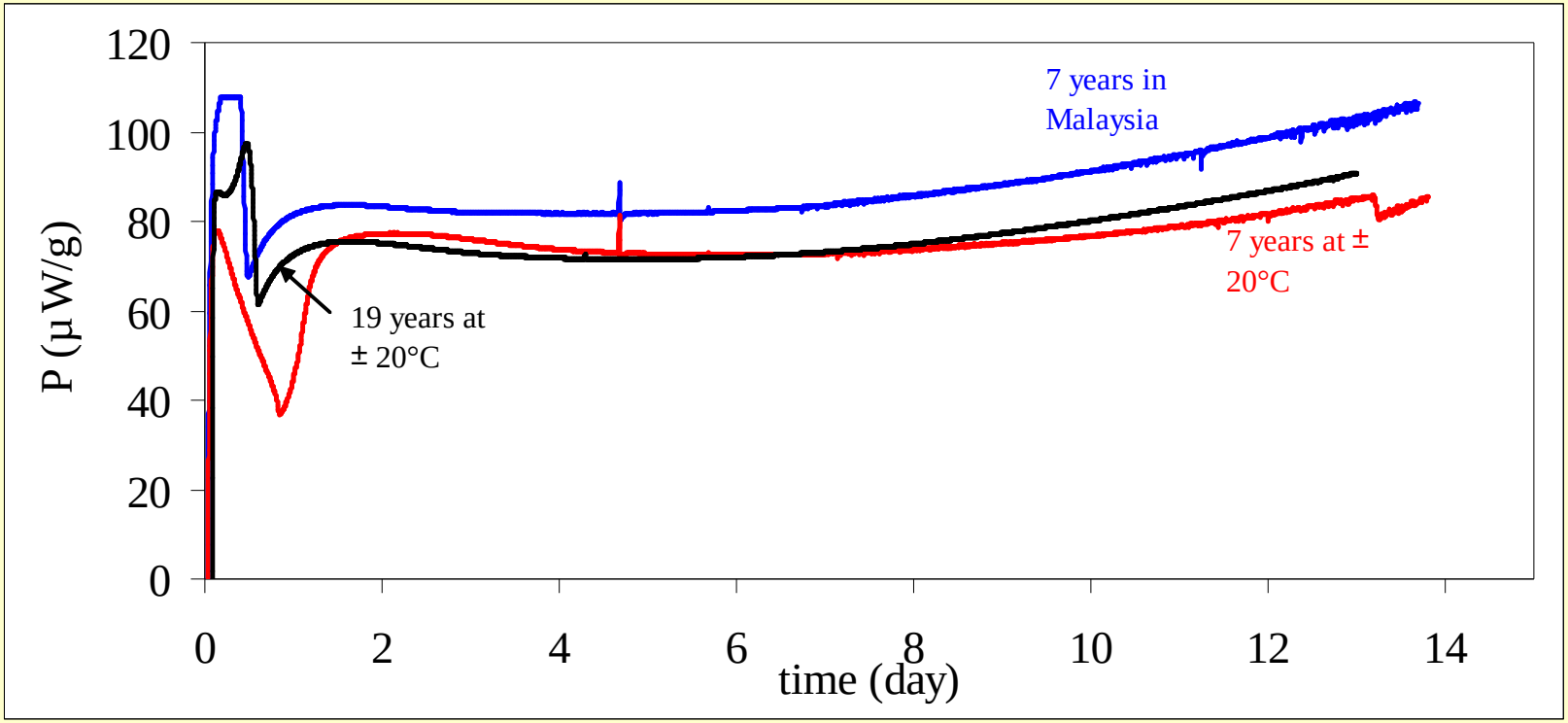
Available results



Result: Simulation of a propellant using kinetic parameters from a similar propellant

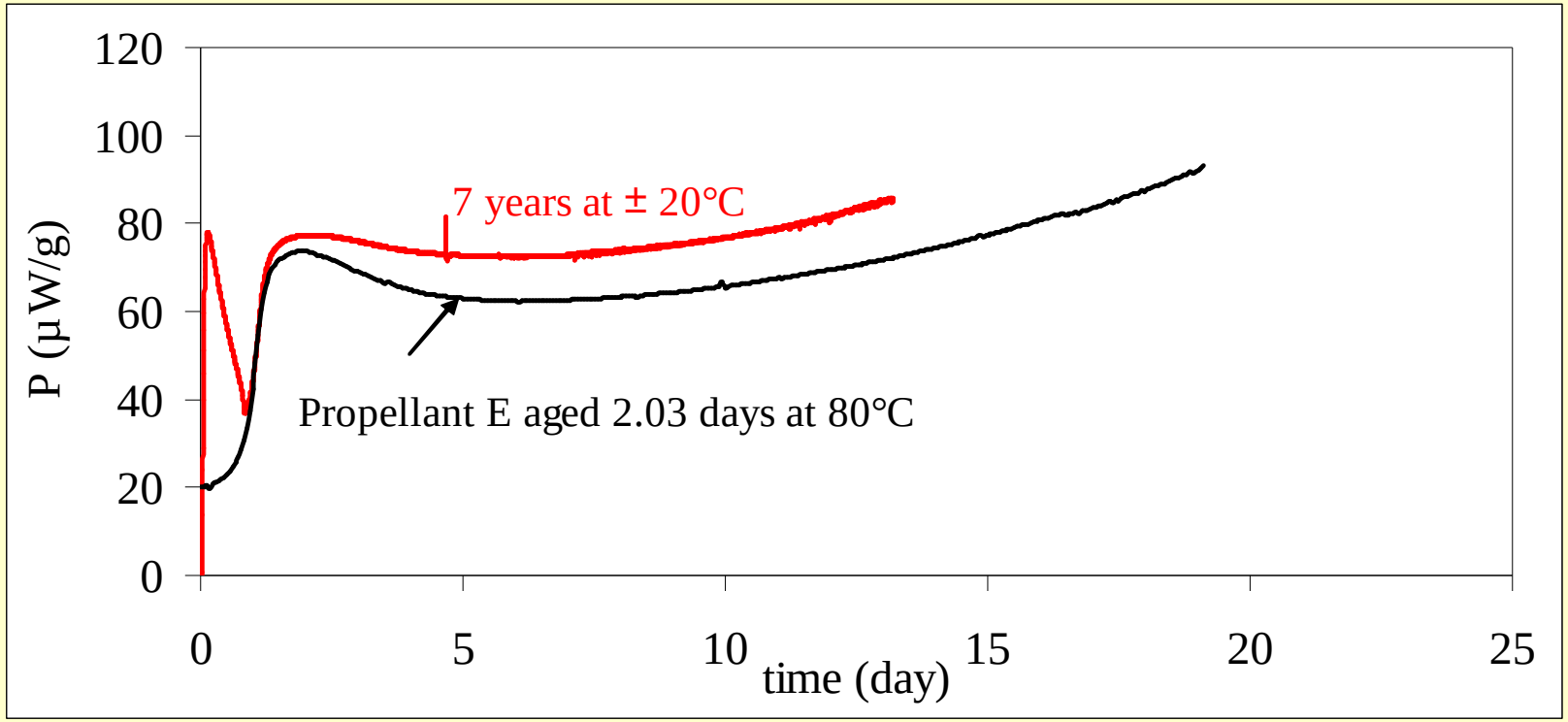
Determination of the parameters used in the simulation

	% Ngl	% DPA	% N-NO-DPA	% DBP
t_0 + 7 years at 22°C ± 2°C	19.0	0.08	0.64	5.9
Propellant E	19.2	0.49	0.46	5.1

$\Rightarrow$ Use of propellant E for the simulation but need to artificially aged this propellant

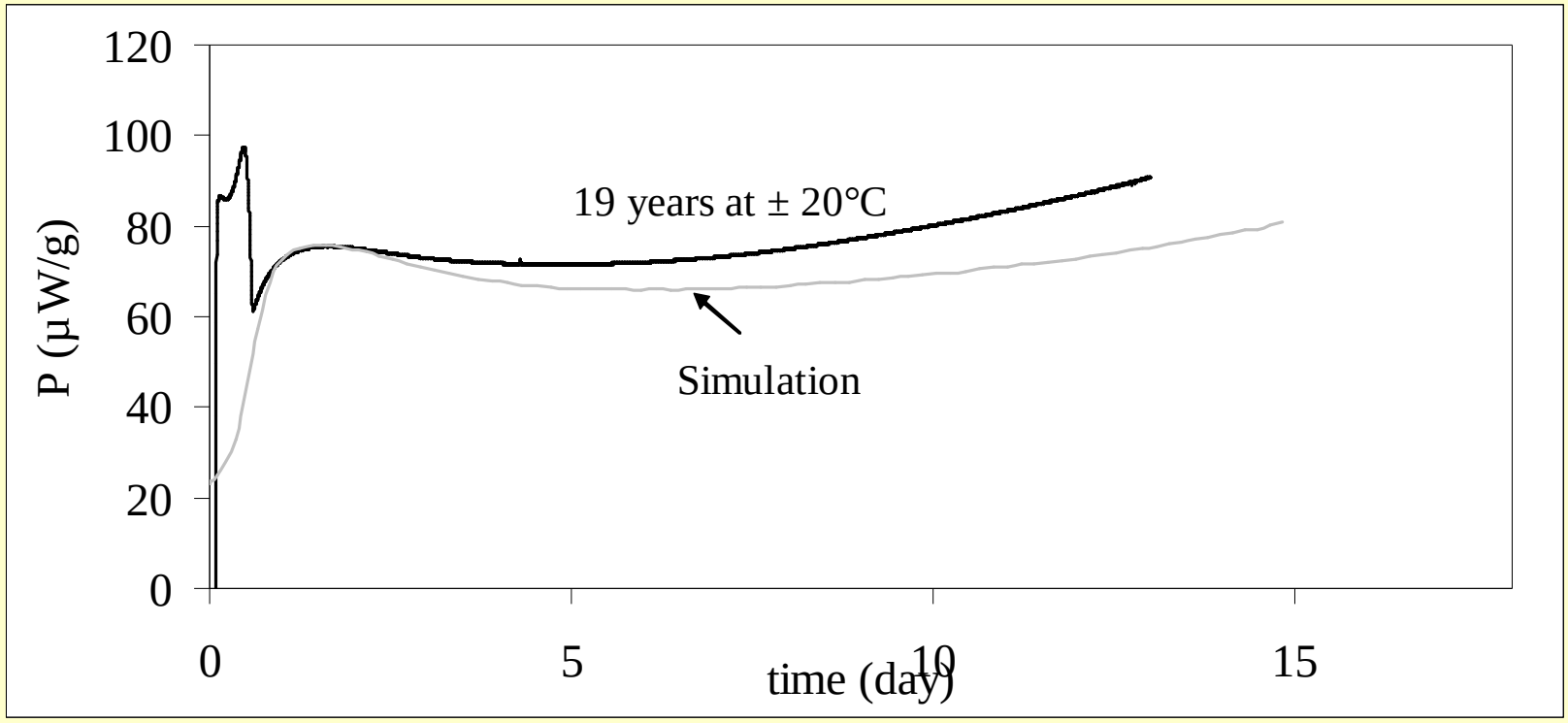
Result: Simulation of a propellant using kinetic parameters from a similar propellant

Determination of the parameters used in the simulation



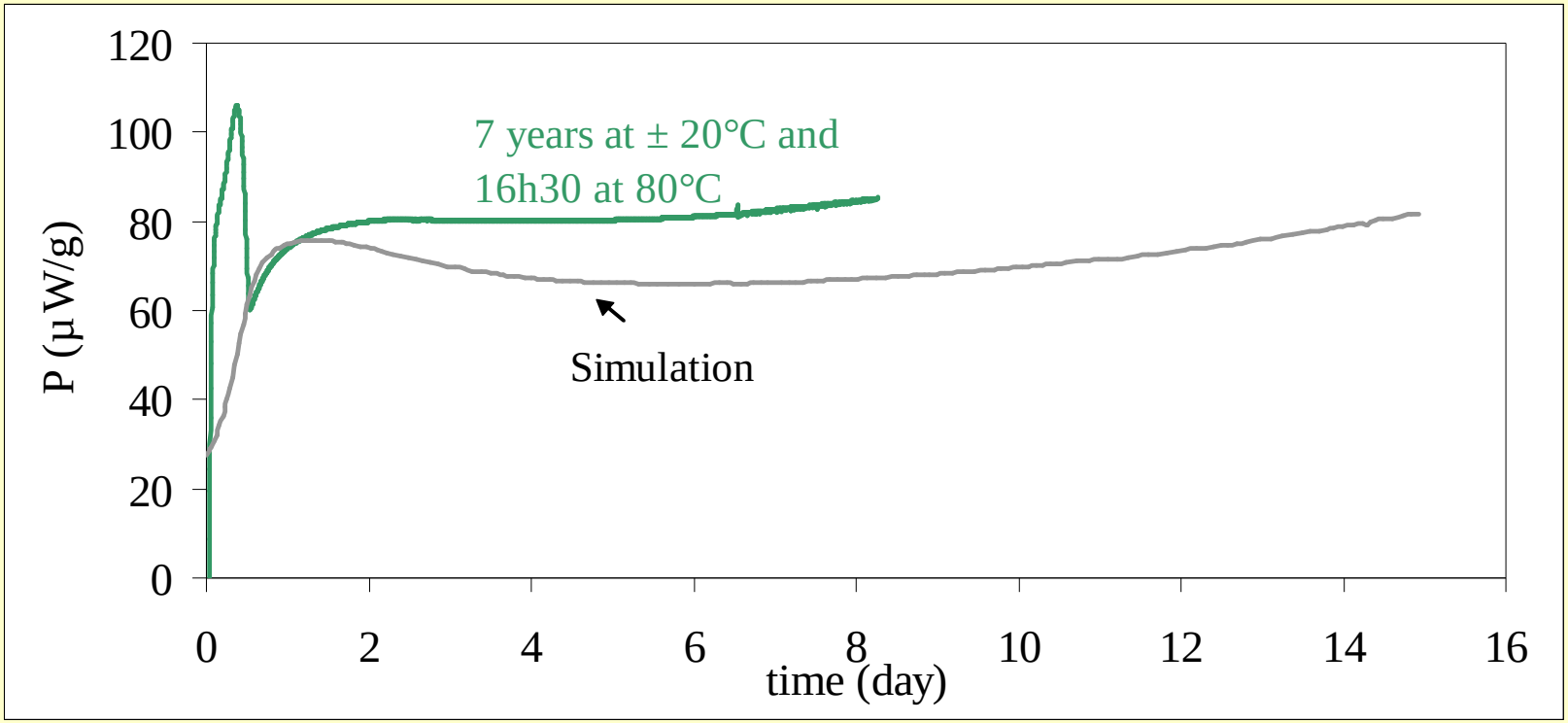
Result: Simulation of a propellant using kinetic parameters from a similar propellant

Simulations



Result: Simulation of a propellant using kinetic parameters from a similar propellant

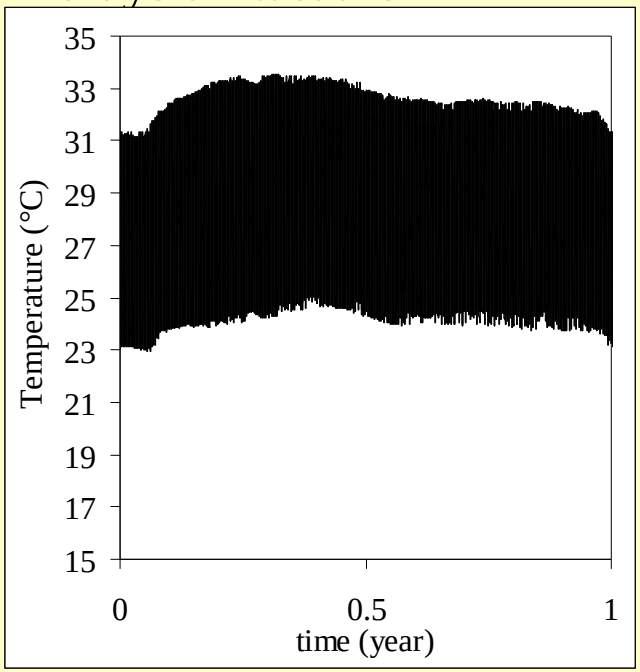
Simulations

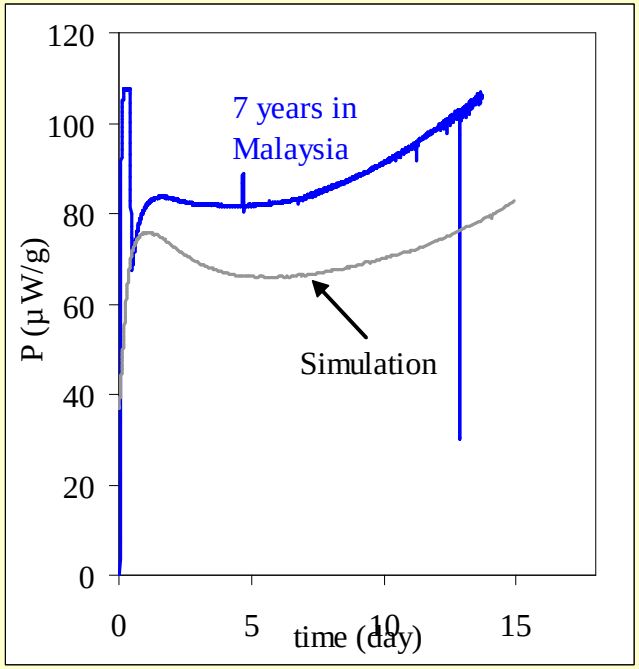


Result: Simulation of a propellant using kinetic parameters from a similar propellant

Simulations

Malaysian weather





Result: Simulation of a propellant using kinetic parameters from a similar propellant

Simulations

- Good correlation of the position of the second maximum
- Less satisfactory correlation of the signal height
- All the simulated curves have lower height than the experimental one
- Discrepancies could arise out of a difference in the propellant moisture

Conclusion

- **HFC measurements of propellant with different nitroglycerin contents**

– The shape of the curve depends on the DBP content
– Kinetics parameters are similar for a nitroglycerin content between 10% and 19%
– Difference of kinetic parameters are observed for higher nitroglycerin content (25.5% and 41.6%)

- **Simulation of a propellant using kinetic parameters from a similar propellant**

– Good correlation between the experimental and simulated curves concerning the position of the second maximum
– Less satisfactory correlation of the signal amplitude
– The differences between the experimental and simulated curve could come from a difference in moisture content between the samples.