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International Meeting on Equipment Qualification
in Nuclear Installations
ÚJV Řež, Czech Republic, May 20–23, 2019

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On determining the uncertainty of activation energy of thermal degradation used for life prediction

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Content

- **Models for thermal life prediction most commonly used**
- **Short description of Arrhenius method of lifetime prediction**
  - Ageing curves and searching the times to the end-point and their uncertainties
  - Arrhenius diagram, its slope (E_A), uncertainty of life prediction and of E_A
- **Sources of E_A uncertainty — determination of uncertainty of:**
  - decisive property and its end-point (elongation at break; el. strength, weight loss)
  - material inhomogeneity (tested batch; long-term production)
  - ~~ageing time~~ and time to the end-point;
  - temperature:
    - thermometers calibration;
    - temperature field inhomogeneity within all specimens in thermal chamber,
    - ~~time inhomogeneity of the temperature~~
- **Degradation (Arrhenius) weighted average temperature** of accelerated thermal ageing — influence of E_A and temperatures; examples

Models for thermal life prediction

- **10-degree (Q_{10}; Van't Hoff's) rule** (1884) can be written like

$$Q_{10} = \left(\frac{k(T_2)}{k(T_1)}\right)^{\frac{10\,°\mathrm{C}}{\Delta T}} \approx 2 \text{ for } \Delta T = T_2 - T_1 = 10\,°\mathrm{C}$$

where $k(T_\mathrm{i})$ is the rate of a chemical reaction at the temperature T_i

- **Arrhenius model** (1912)**:** Rate of a chemical reaction k depends on $1/T$ by the relation

$$k = Ae^{-\frac{E_\mathrm{A}}{\mathrm{k_B}T}} \quad \Rightarrow \quad t_1 = t_2 \cdot e^{-\frac{E_\mathrm{A}(T_2 - T_1)}{\mathrm{k_B}T_1 T_2}}$$

- Arrhenius equation relates simulated service life t_2 at the temperature T_2 [K] of a material with the time t_1 of its accelerated thermal ageing at the temperature T_1.

Arrhenius model for thermal life prediction

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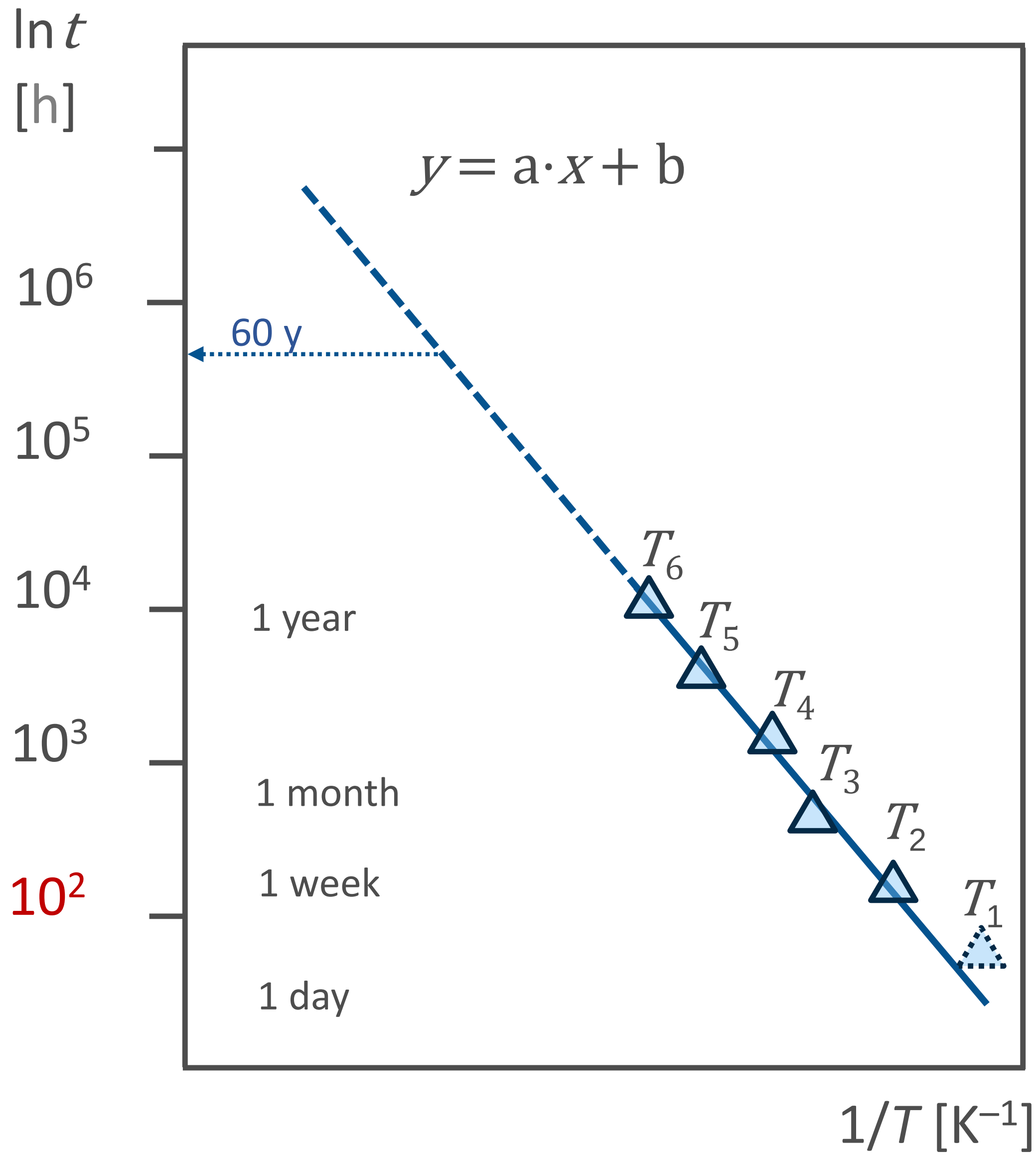
- **Activation energy E_A of thermal degradation is proportional to the slope a of the plot in the $(x\,;\,y)$ coordinates**

$(x = 1/T;\ y = \ln t)$

$$\ln t = a \cdot (1/T) + b$$



Arrhenius model for thermal life prediction

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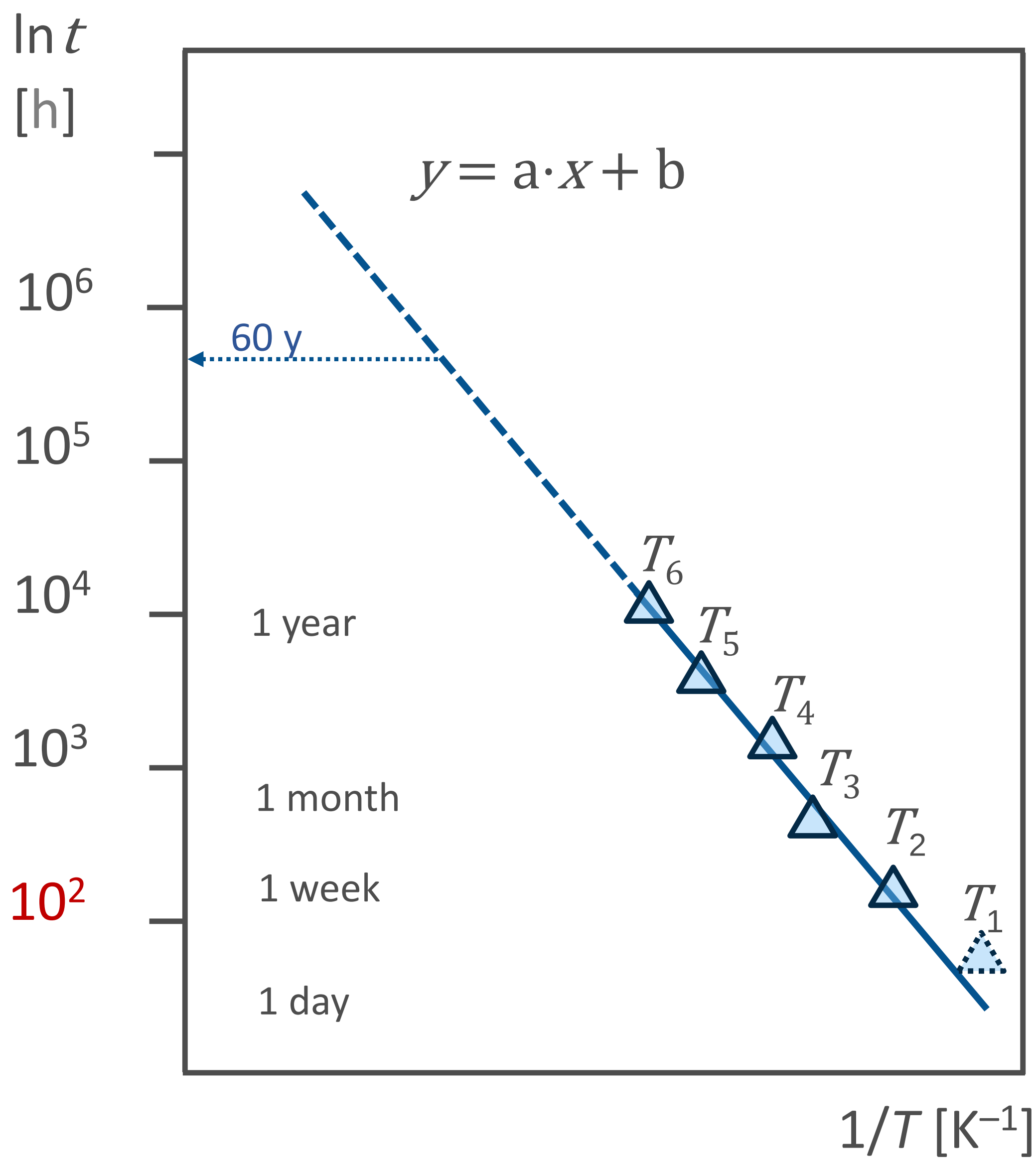
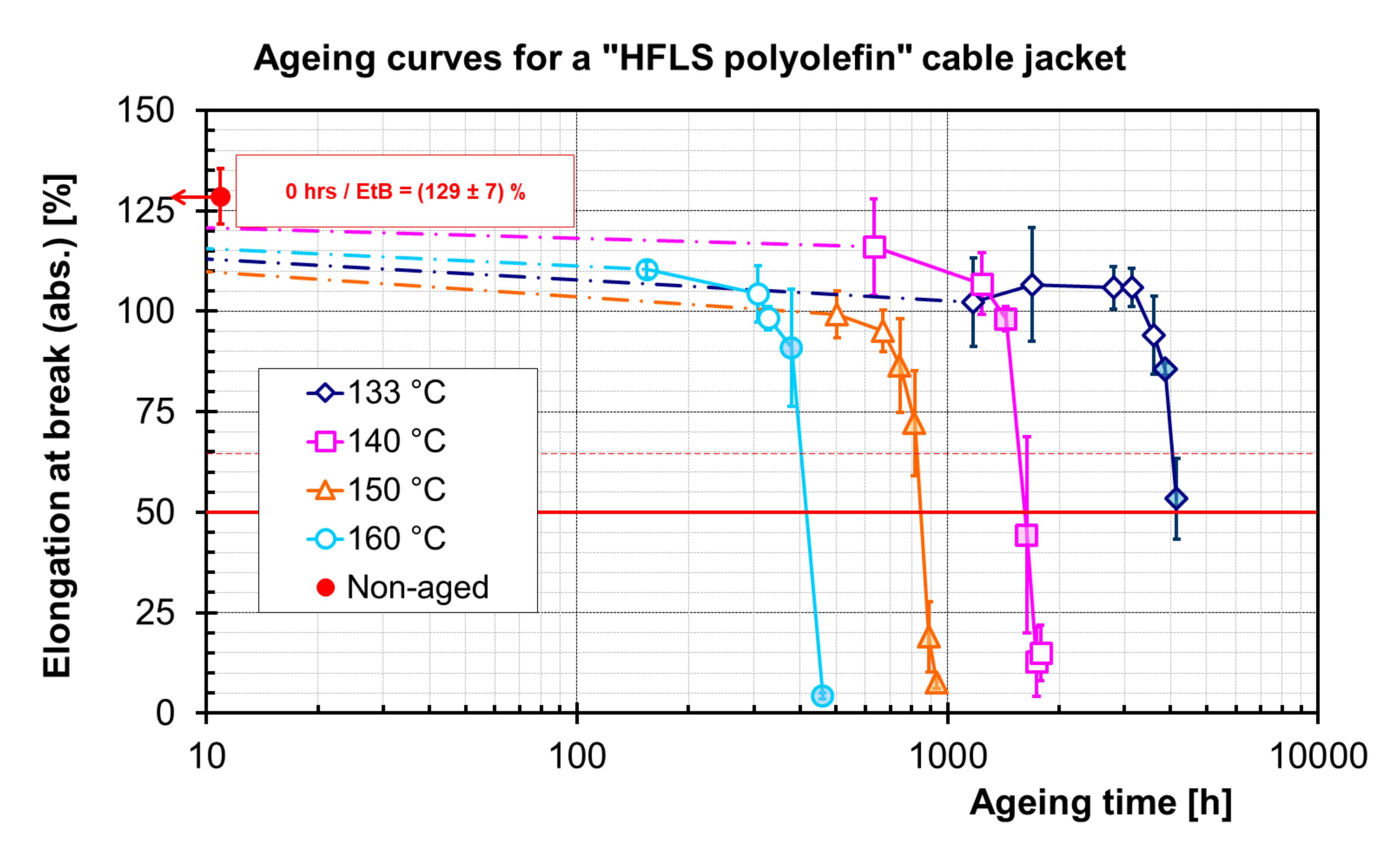
T_i — ageing temperature
i ≥ 3 (commonly 4 to 6);

$T_i - T_{i+1} \geq 10\ \mathrm{K}$
(recommended)



Ageing curves determination



Finding the time to the end point and its uncertainty

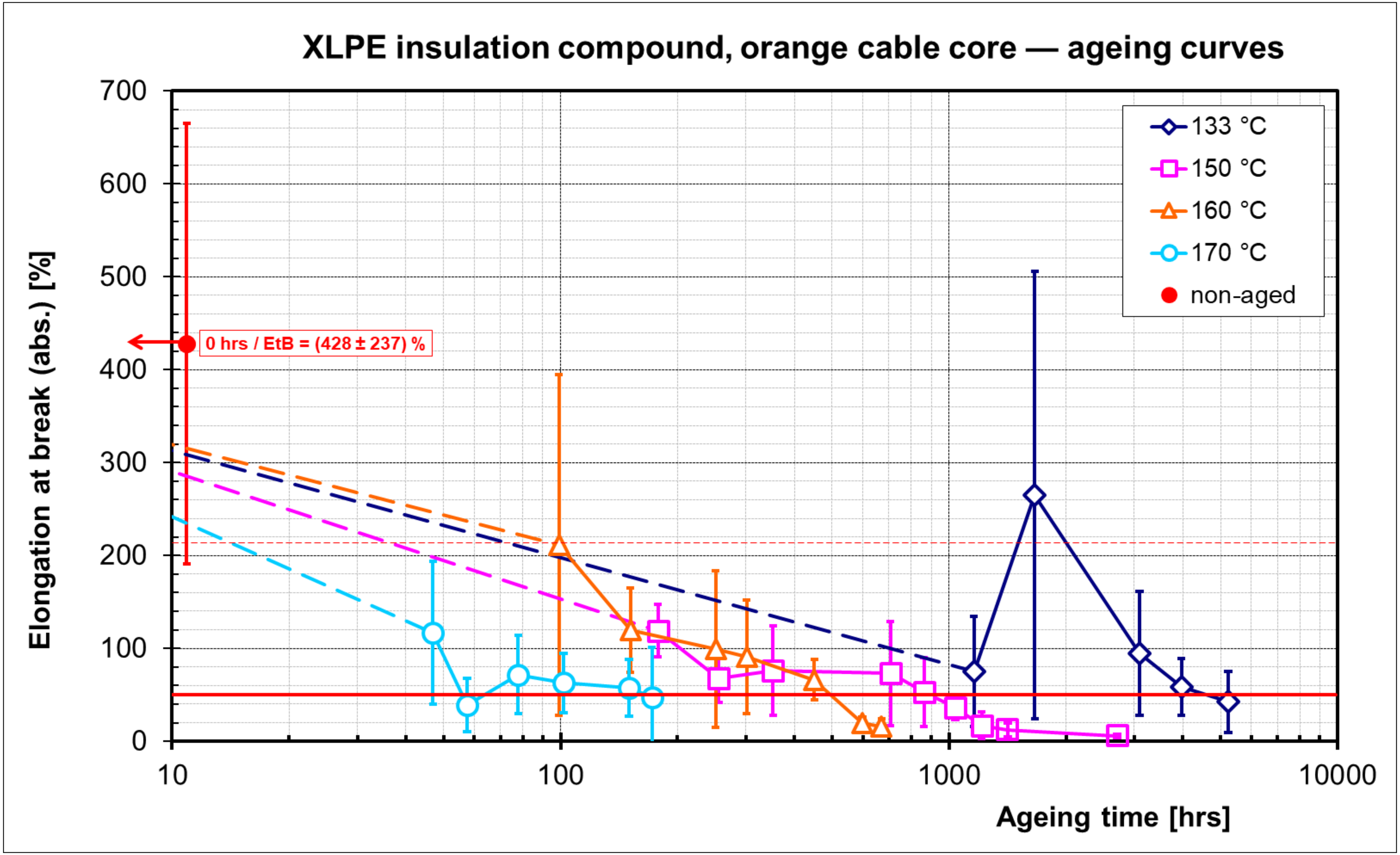
- **Ageing curves have to be fitted to find the time to the end-point**
  - Usually relative decrease (eventually rel. increase) of to-the-ageing sensitive and functional property to 50 % of its original value
  - E.g., for elongation at break, the **linear regression** in the transition region is recommended, or the fitting by a sigmoidal curve can be performed
  - The standard deviation (s.d.) of the slope s_a of a linear regression line is not given in the MS Office 365 Excel SW. (Only function „=SLOPE(y; x)“ is available.)
  - The s.d. of the slope s_a

    has to be calculated by the relation: $s_a = \sqrt{\dfrac{\frac{1}{n-2}\sum_{i=1}^{n}\hat{\varepsilon}_i^2}{\sum_{i=1}^{n}(x_i-\bar{x})^2}}$

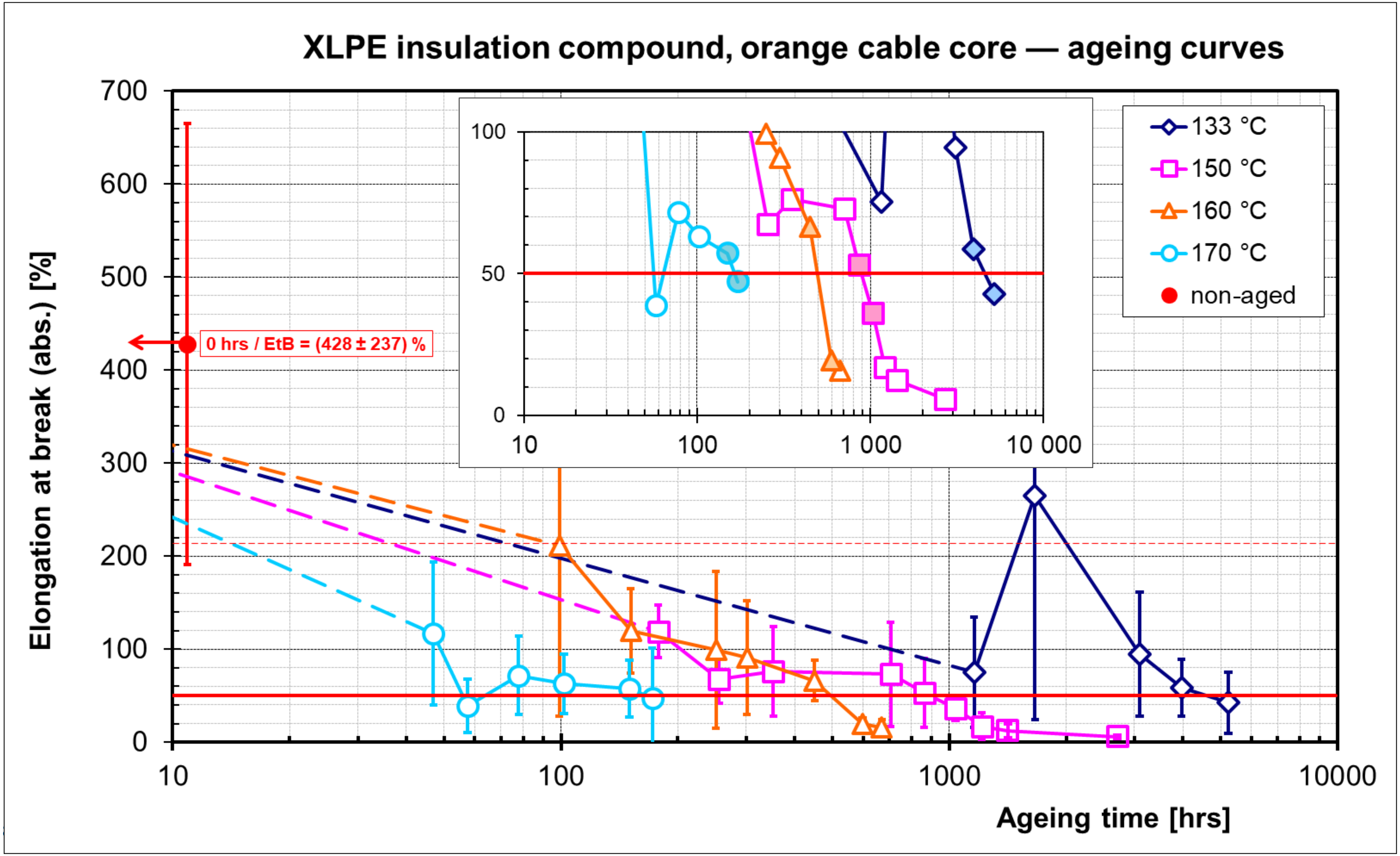
  where the term $\sum \varepsilon_i^2 = \sum_i (y_i - b - a \cdot x_i)^2$ is called „**sum of residuals**“,

  and the degree of freedom is n – 2. The n is the number of all data points, i.e., of all specimens used for regression line determination. The quantity s_a is not the same as the quantity „the s.d. of linear regression s_r^2“ which serves to the determination of s.d. of the predicted value y_{pred} for a given value of x_{set}.

Ageing curves, other example



Ageing curves, other example



Ageing curves, other example of smoothing

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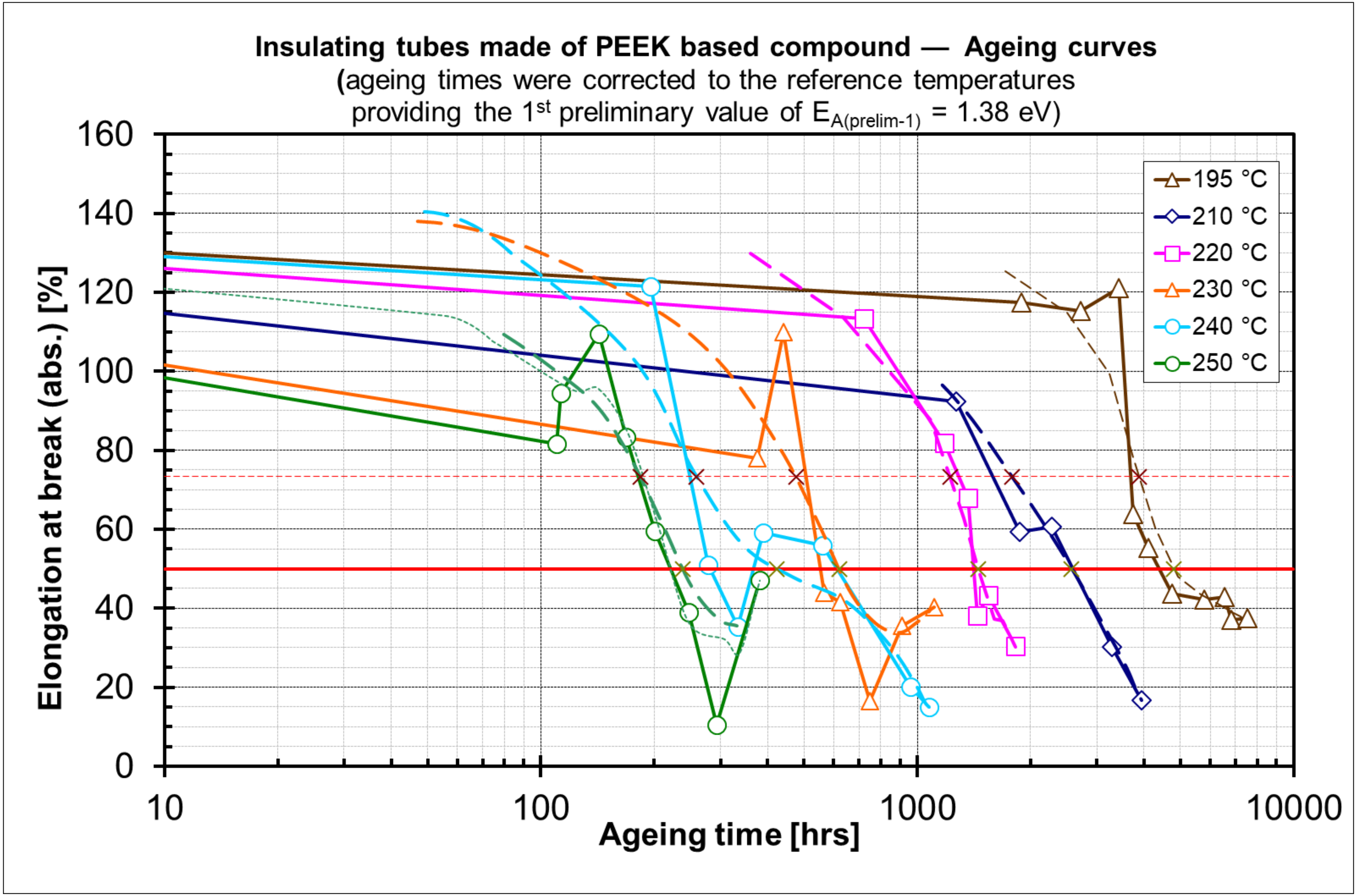


Finding the time to the end point and its uncertainty

Standard deviation $s_r^2 = \frac{1}{n-2} \cdot \sum_i (y_i - b - a \cdot x_i)^2$ (in the Excel „=STEYX(y; x))

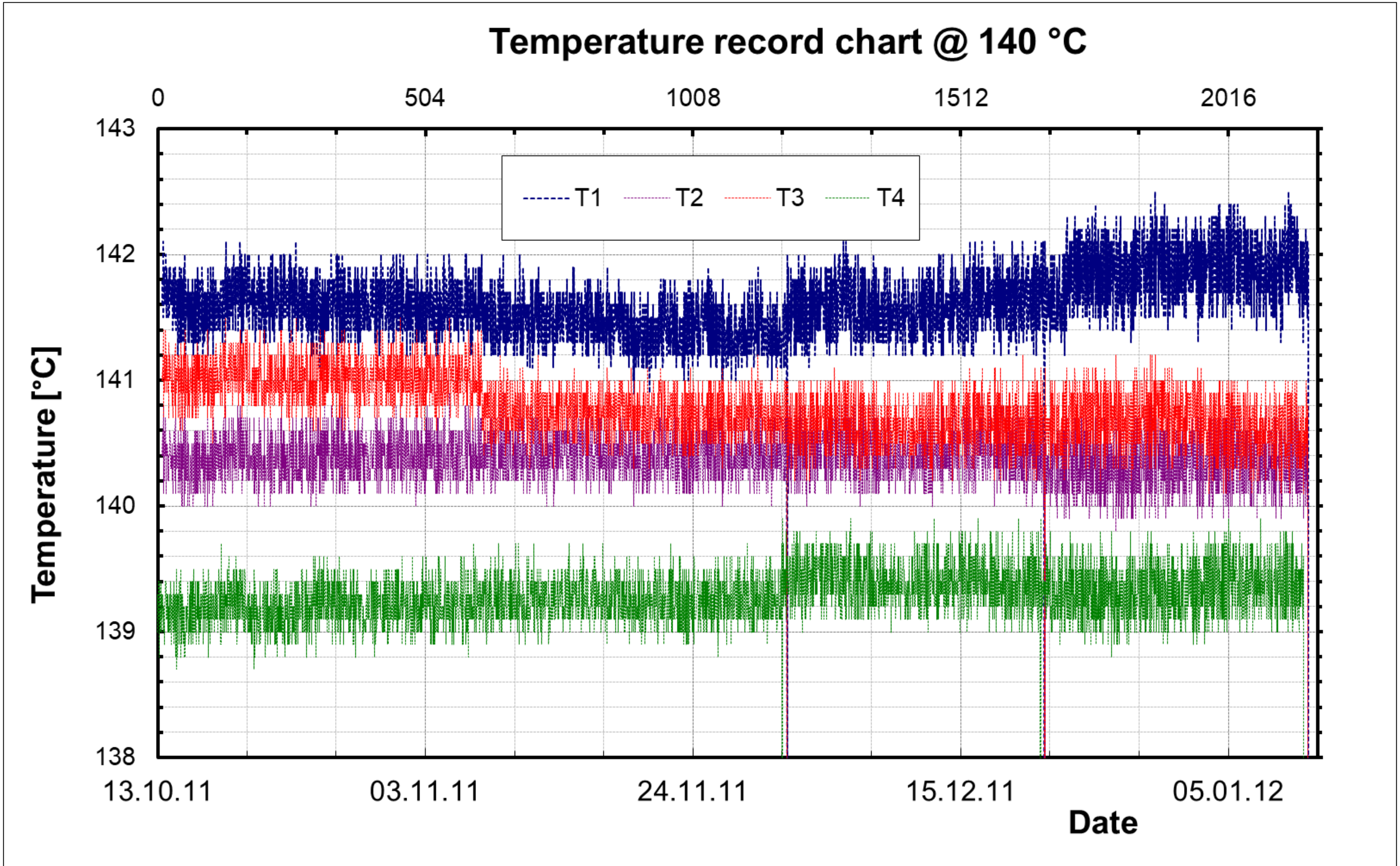
of the linear regression line serves to determination of predicted value y_{pred} for a given value of x_{set}

$$s_{y_{pred}} = \frac{s_r}{\sqrt{n}} \cdot \sqrt{n + 1 + \frac{\left(x_{set} - \overline{x}\right)^2}{\left(\overline{x^2} - \overline{x}^2\right)}}$$

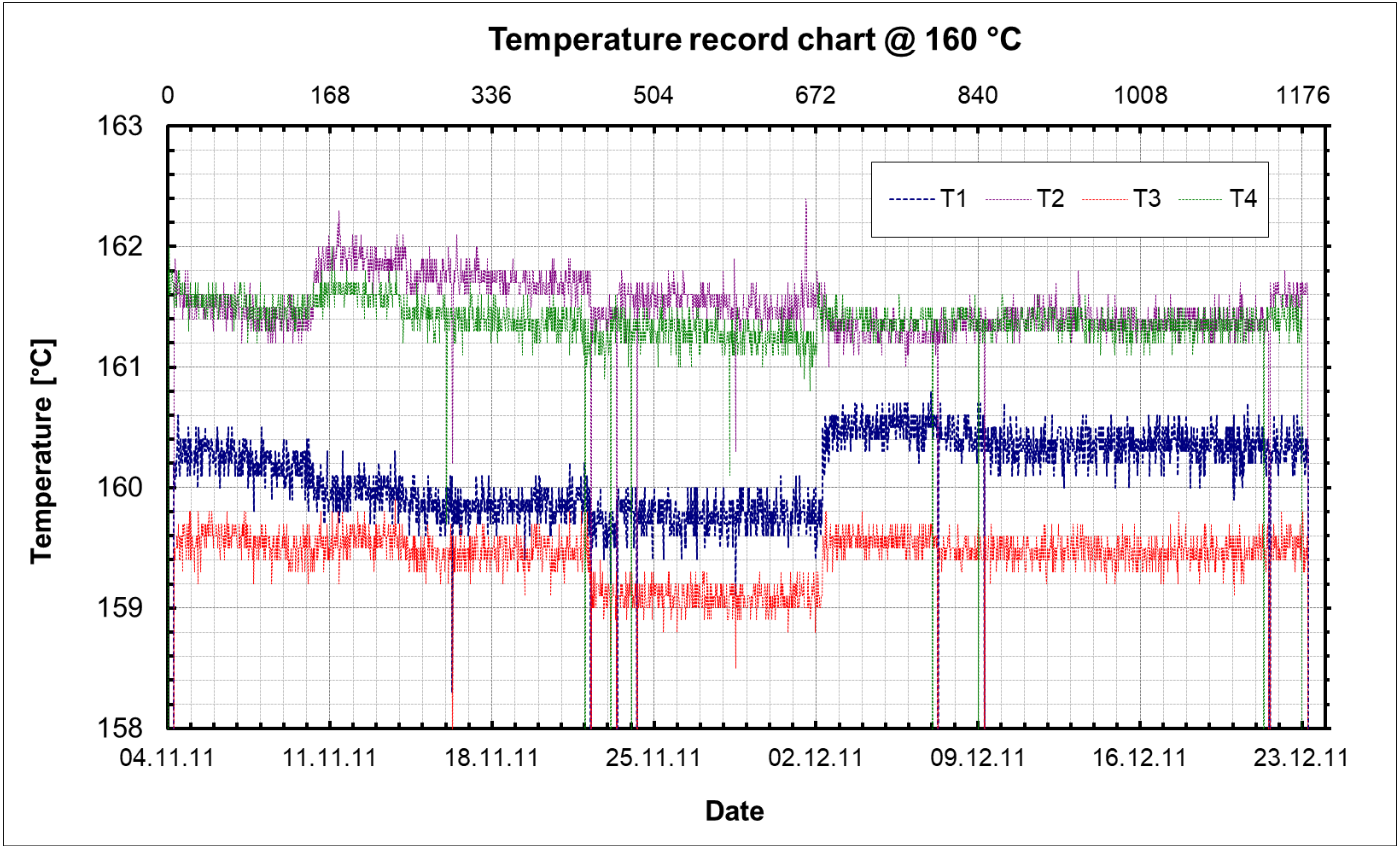
The uncertainty of time to the end point (in logarithmic (ln) scale) for the given x_{set} can be determined by the relation

$$s_{\ln t} = \frac{1}{\mathrm{a}} \cdot s_{y_{pred}} \quad ?(s_{\ln t} \doteq \frac{1}{\mathrm{a}} \cdot s_{y_{pred}})?$$

Evaluation of thermal ageing records, finding the Arrhenius weighted (degradation equivalent) average temperature



Evaluation of thermal ageing records, finding the Arrhenius weighted (degradation equivalent) average temperature



Arrhenius weighted (degradation equivalent) average temperature T_{Arrh} — Calculation relation

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$$T_{\mathrm{Arrh}} = \frac{E_{\mathrm{A}}}{k_{\mathrm{B}}} \frac{1}{\ln \dfrac{\sum_{i=1}^{n} t_i}{\sum_{i=1}^{n} t_i \, e^{-\frac{E_{\mathrm{A}}}{k_{\mathrm{B}} T_i}}}} = -\frac{E_{\mathrm{A}}}{k_{\mathrm{B}}} \left[\ln \left(\frac{1}{t} \sum_{i=1}^{n} t_i \, e^{-\frac{E_{\mathrm{A}}}{k_{\mathrm{B}} T_i}} \right) \right]^{-1}$$

where $t = \sum_{i=1}^{n} t_i$ **,**

t_i **, resp.** T_i **— the time, resp. the temperature, in the** i-th **section of ageing**

Arrhenius weighted average temperature, sensitivity to E_A and temperature, examples

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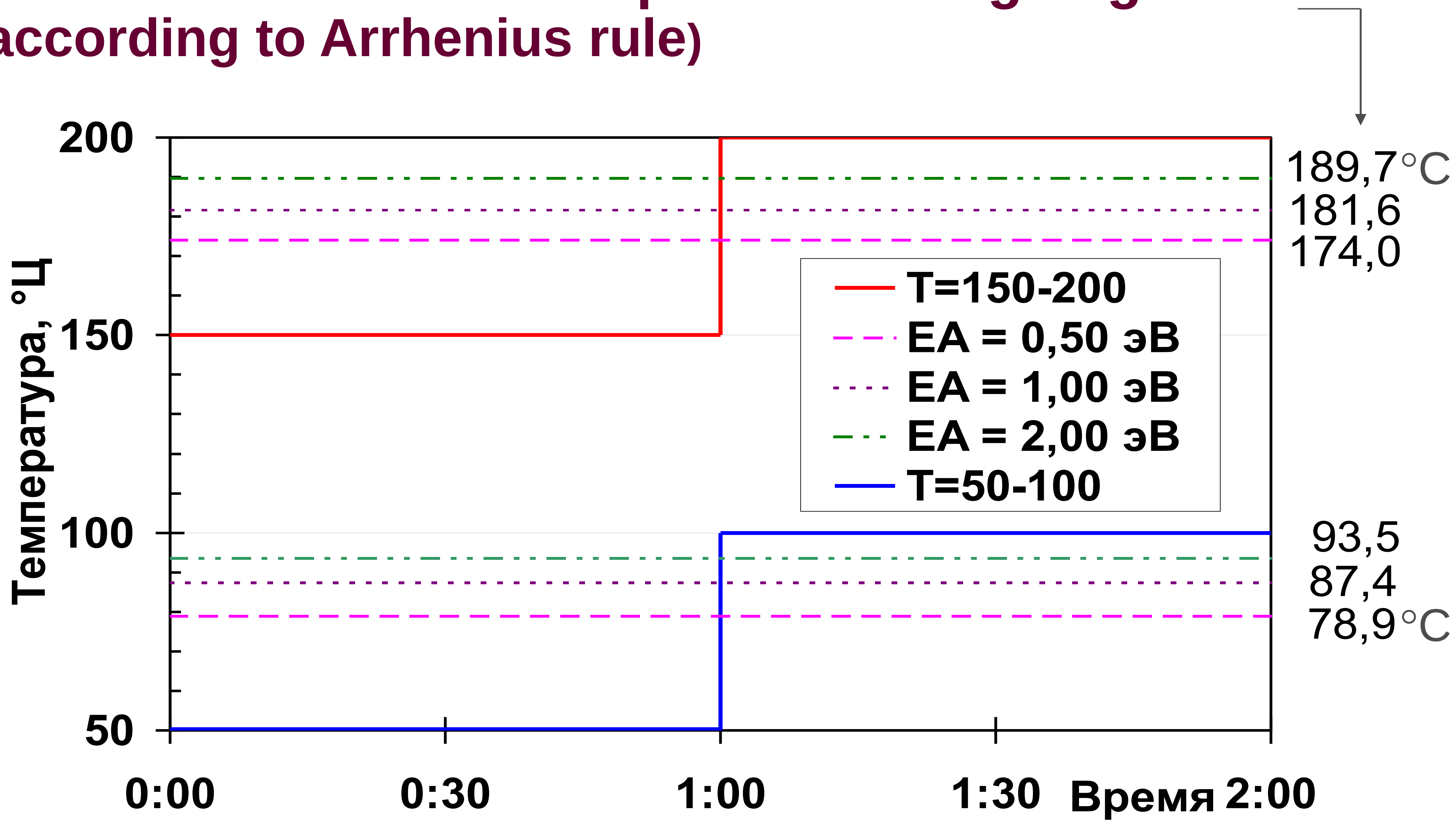
Calculation of mean temperature of ageing
(according to Arrhenius rule)



Lifetime prediction and its sensitivity to E_A, examples

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Determination of service life from the lifetime plot — calculation of uncertainty of extrapolation

Input data:

E_A =1,09 eV (±0,10 eV)

T_1 = 135,0 °C (±1,2 °C)

T_2 = 60 °C (±0,5 °C)

t_1 = 14 days (336 hrs),

t_2 = ?? service life ??

Calculation:

Normal distribution of service life:

$t_2 = 41 \pm 29$ years

Logarithmic-normal distribution of service life:

$t_2 = 41^{+42}_{-21}$ years

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Calculation of mean temperature of ageing (according to Arrhenius rule)

- **Effect of activation energy:**
  Higher activation energy results in higher Arrhenius average temperatures. But for low temperature differences (≈ 1 °C and the less), the effect is insignificant.
- **Effect of temperature shift:**
  Increasing temperature shift reduces Arrhenius average temperatures.
- **Effect of overheating: Even relatively short-term overheating increases the Arrhenius average temperature substantially. But the short-term temperature decrease is insignificant.**

Arrhenius weighted average temperature — elimination of time inhomogeneity of ageing temperature

- **The problem (?):**
  The activation energy is not known before the measurement!
- **The solution (!):**

1. As a preliminary value of E_{A0}, use any temporary one known from similar materials, from last measurements, or try to guess it. Or use, e.g., EA = 1.00 eV.
2. Calculate Arrhenius weighted average temperatures (AWAT) of thermal ageing individually for all ageing temperatures and for all aged batches.
3. Determine the Arrhenius plot and calculate the second preliminary value of E_{A1}, while all ageing time are related/recalculated to the reference temperatures of ageing T_i, $i = 1$ to n, where n is here the number of ageing temperatures.
4. Repeat the iteration loop until, e.g., $|E_{Aj} - E_{Aj+1}| \leq 0.005$ eV.
   (The beginning of the second iteration from the step 3 is sufficient in comparison to a relatively low sensitivity of AWAT to EA value.)

Arrhenius plot — examples

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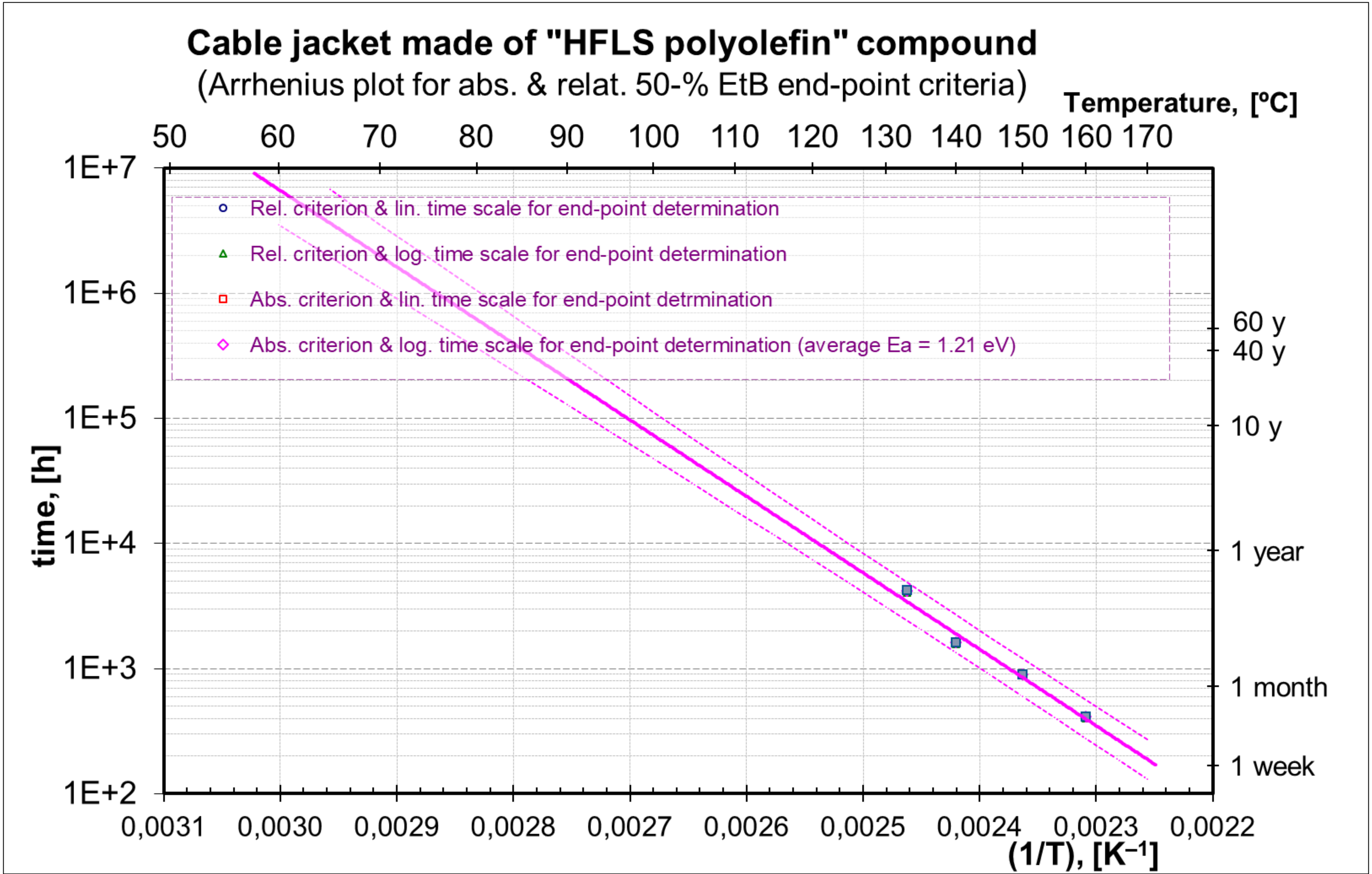

Arrhenius plot — examples

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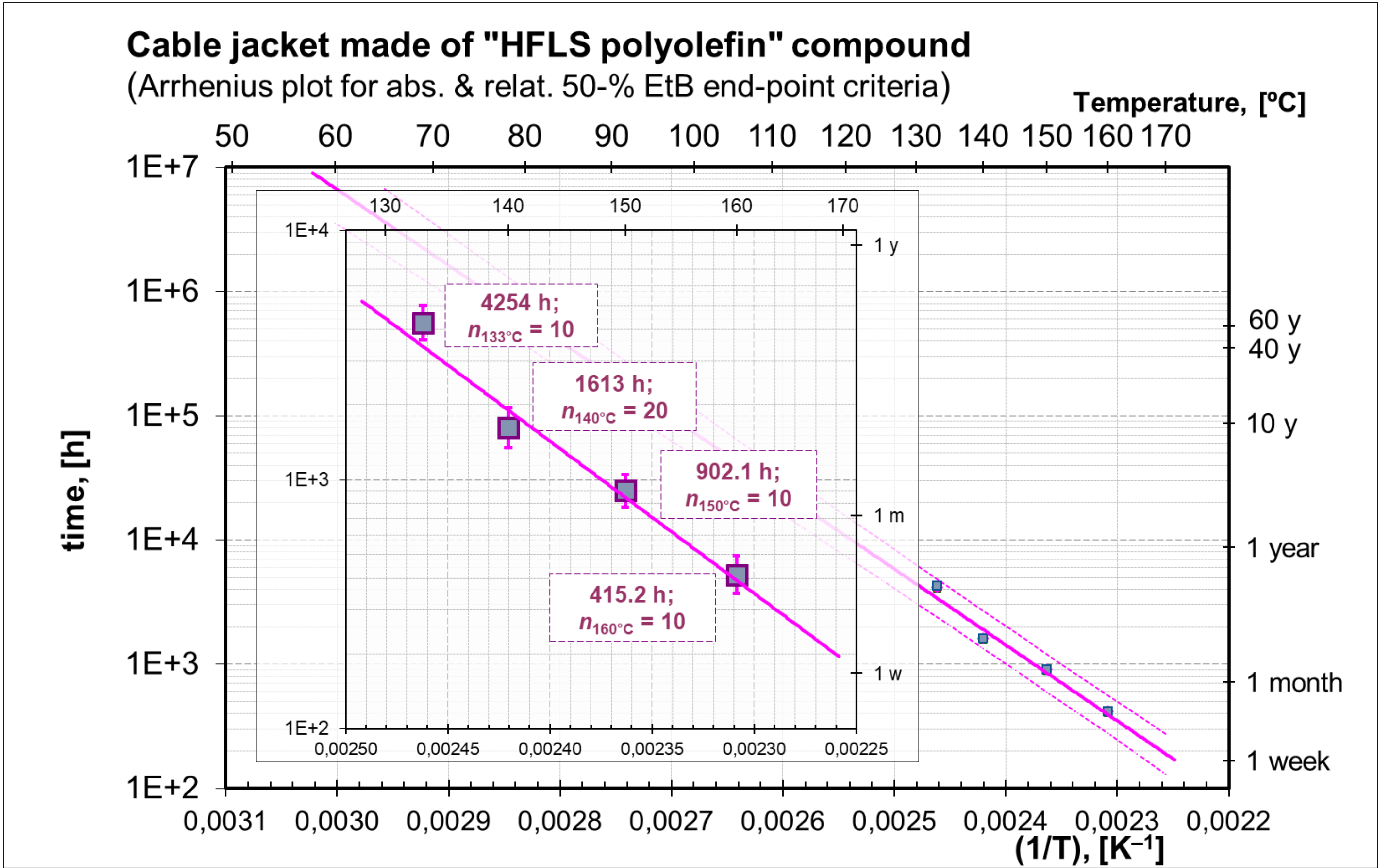
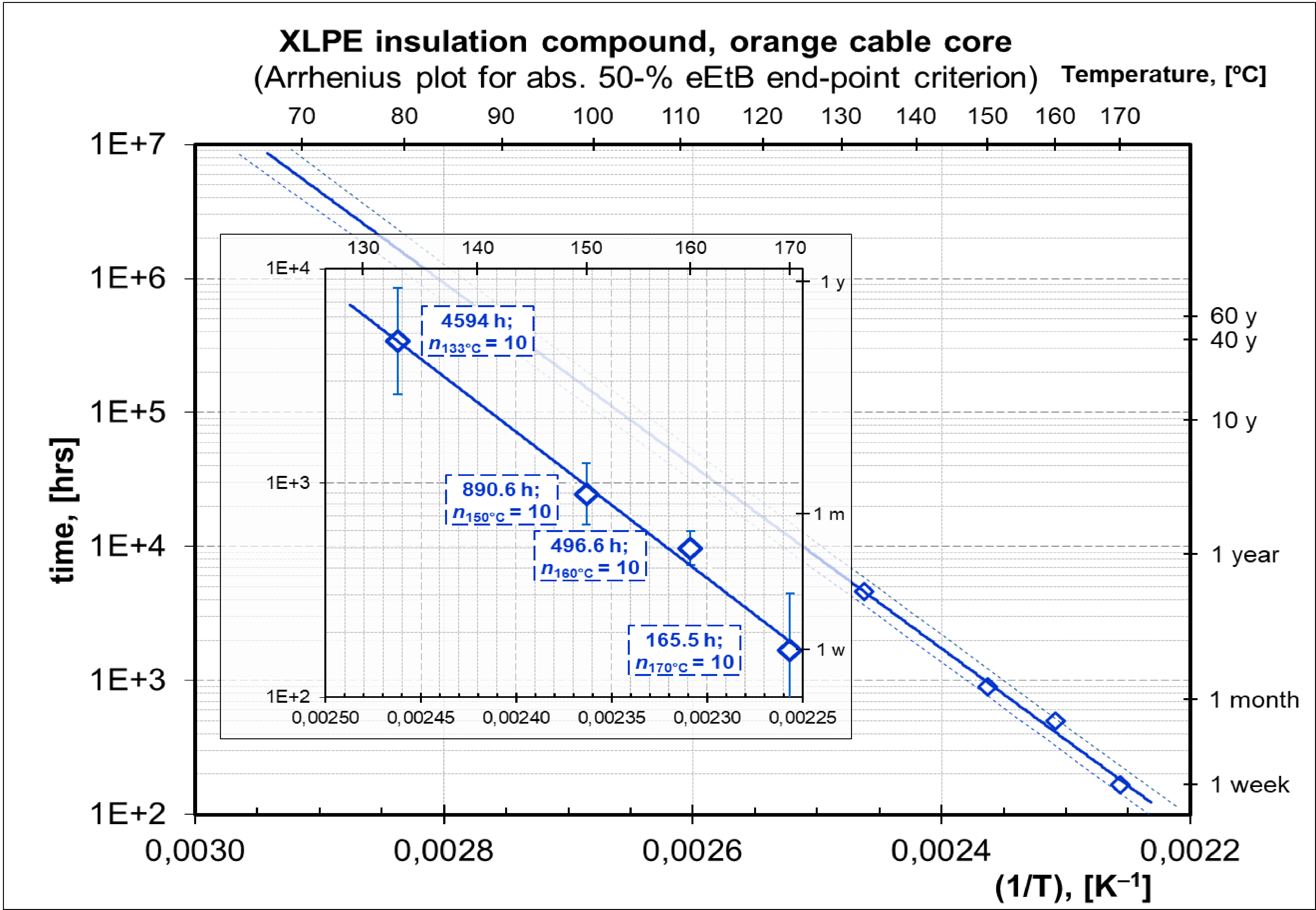


Arrhenius plot — examples



Arrhenius plot — examples

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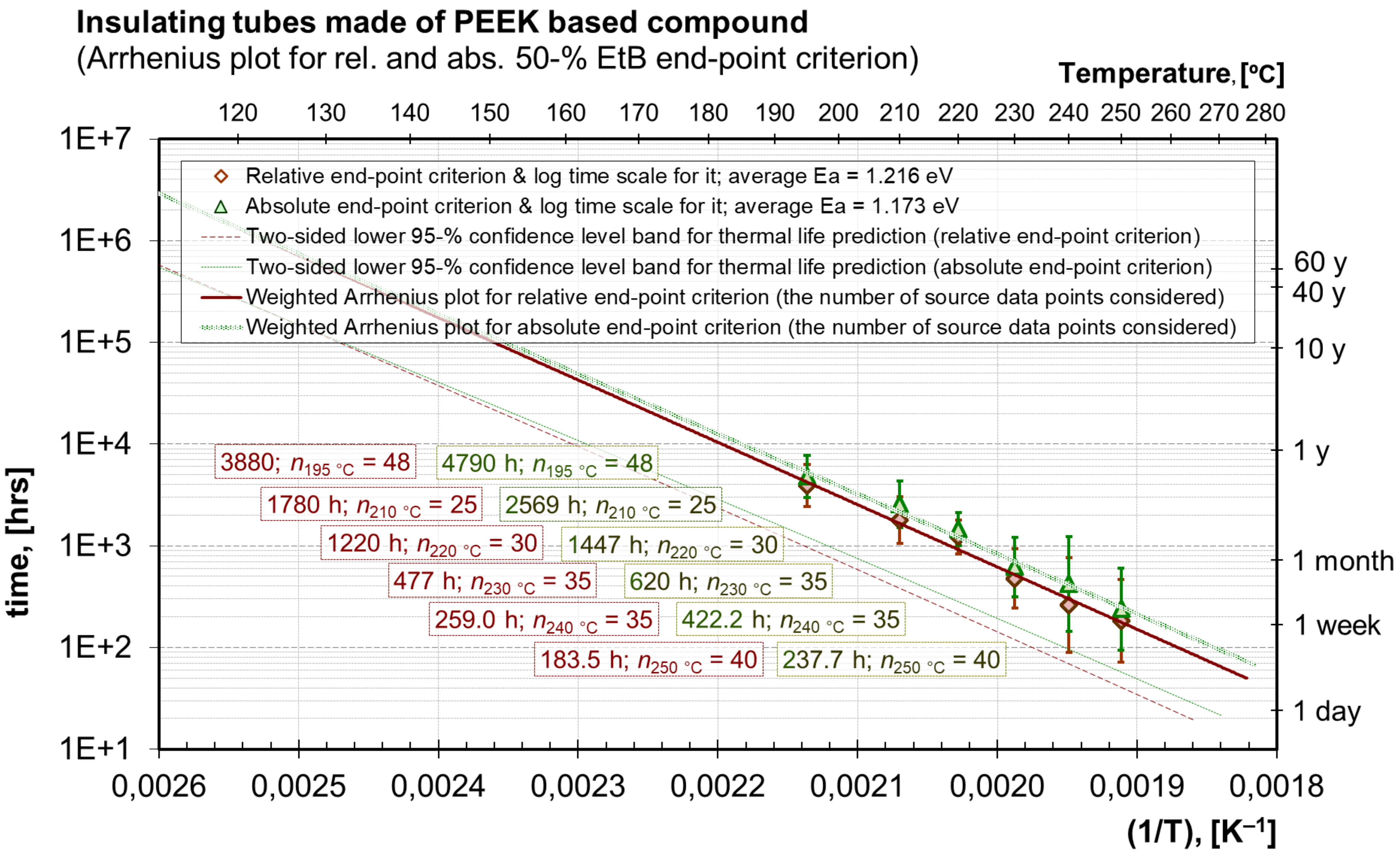

Conclusions

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- **It was presented the iterative method eliminating the time variance of temperature during thermal ageing for life prediction by Arrhenius method**
- **The large sources of EA determination are:**
  - The temperature field inhomogeneity
  - The variance among production batches
- **The complete eliminating the time variance of temperature during thermal ageing decreses the total EA uncertainty mainly when many ageing breaks are applied (black-outs, specimen manipulations, etc.)**

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Discussion

Thank you for attention!

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