

To Reduce GUM's Recommendations to Practice

Structure of Contributions to Combined Standard Uncertainty

“Uncertainty Concepts in Thermo-Physical Measurement Methods”

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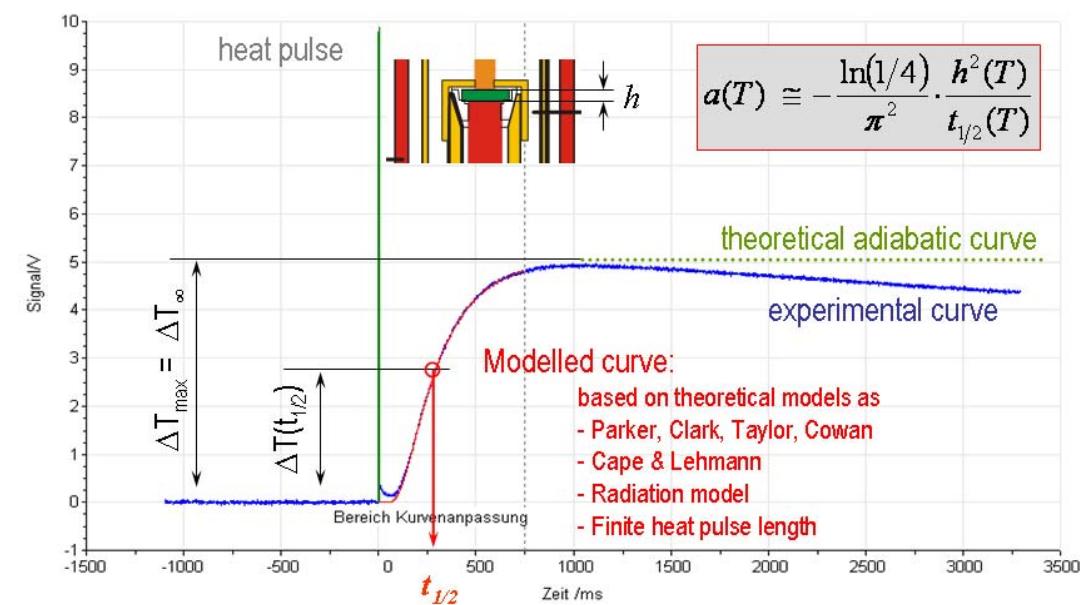
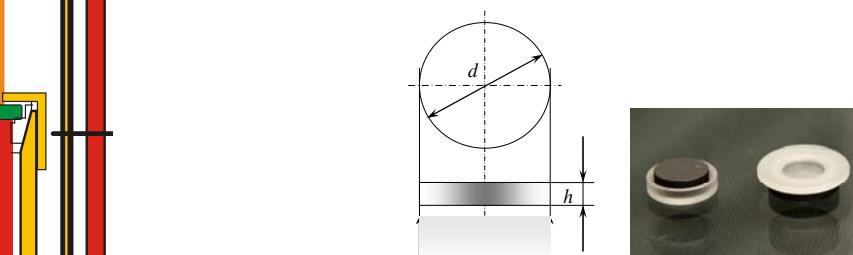
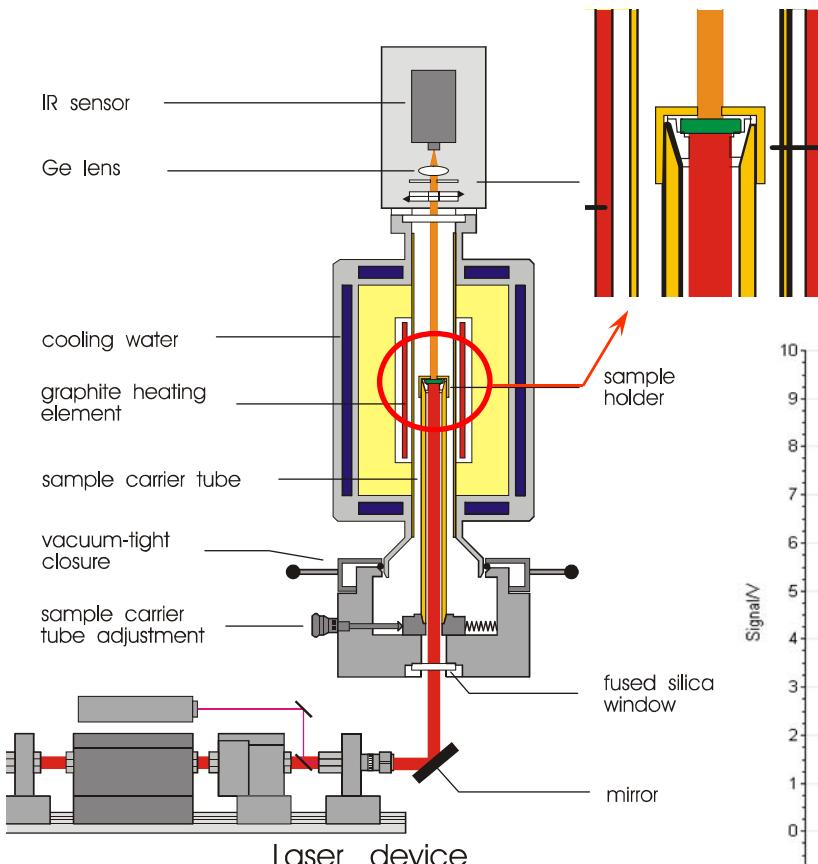
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 - Push Rod Dilatometry
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- Summary

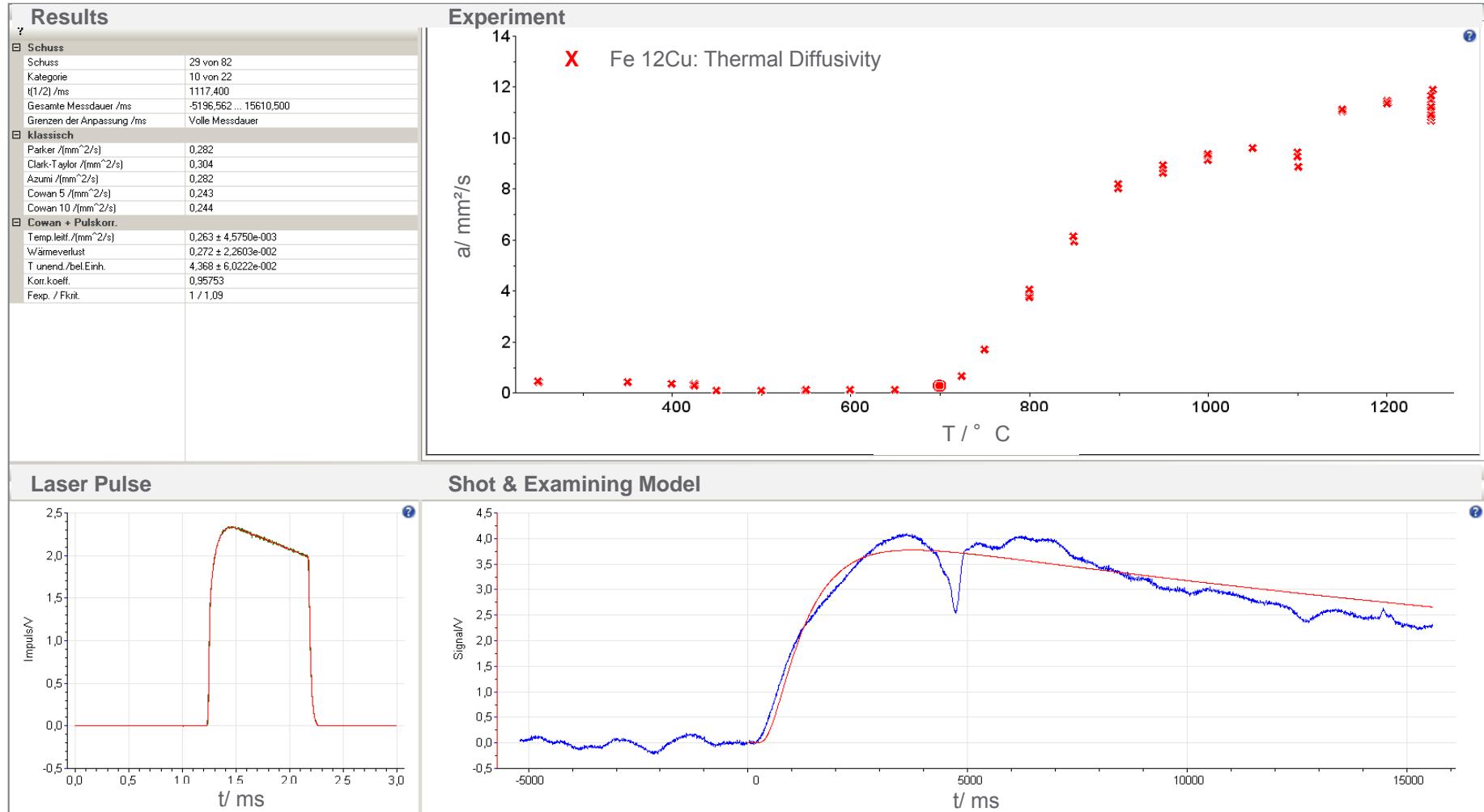
Motivation

... Basics and Ideal Conditions



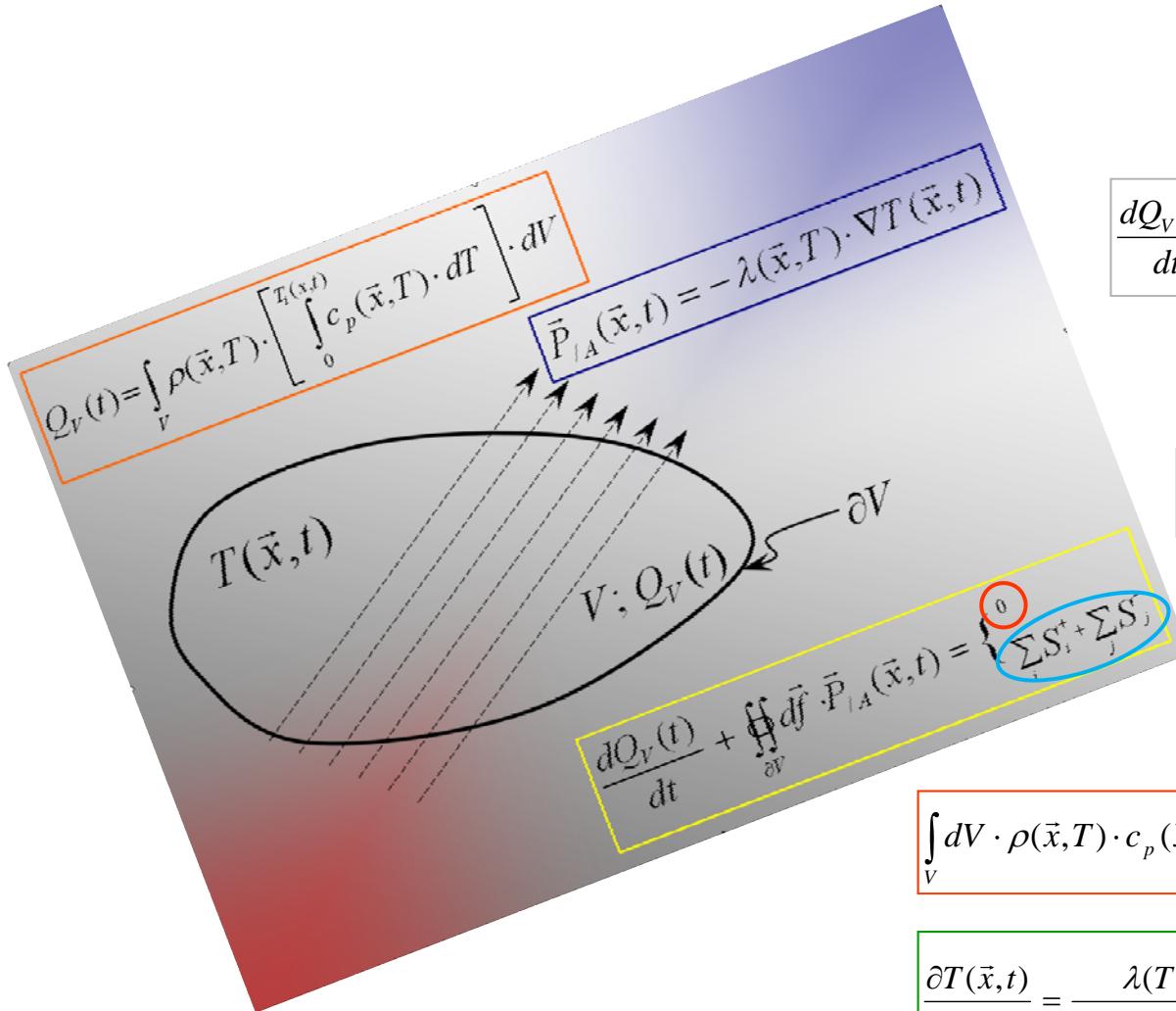
Motivation

... Ideal Conditions ???



Motivation

... Phenomenology meets Physics – and Physics meets Maths



Change of Heat Content

$$\frac{dQ_V(t)}{dt} = \frac{\partial}{\partial t} \int_V \rho(\vec{x}, T) \cdot \left[\int_0^{T_i(\vec{x},t)} c_p(\vec{x}, T) \cdot dT \right] \cdot dV$$

Heat Flux

$$\oint_{\partial V} d\vec{f} \cdot \vec{P}_A(\vec{x}, t) = - \oint_{\partial V} d\vec{f} \cdot \lambda(\vec{x}, t) \cdot \nabla T(\vec{x}, t)$$

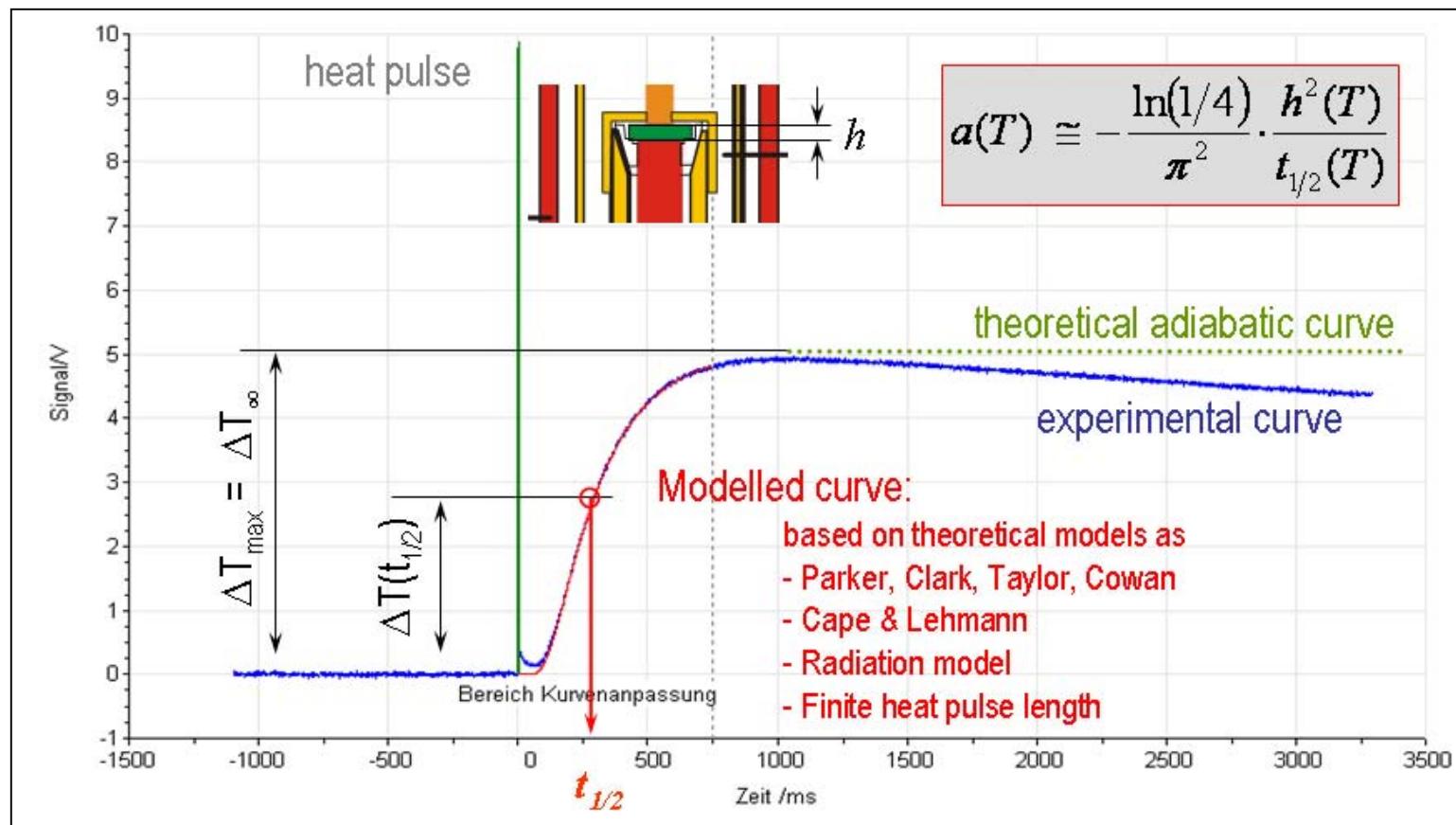
Thermal Balance of a
Conservative System

$$\int_V dV \cdot \rho(\vec{x}, T) \cdot c_p(\vec{x}, T) \cdot \frac{\partial T(\vec{x}, t)}{\partial t} - \oint_{\partial V} \lambda(\vec{x}, T) \cdot \nabla T(\vec{x}, t) \cdot d\vec{f} = 0$$

$$\frac{\partial T(\vec{x}, t)}{\partial t} = \frac{\lambda(T)}{\rho(T) \cdot c_p(T)} \cdot \Delta T(\vec{x}, t)$$

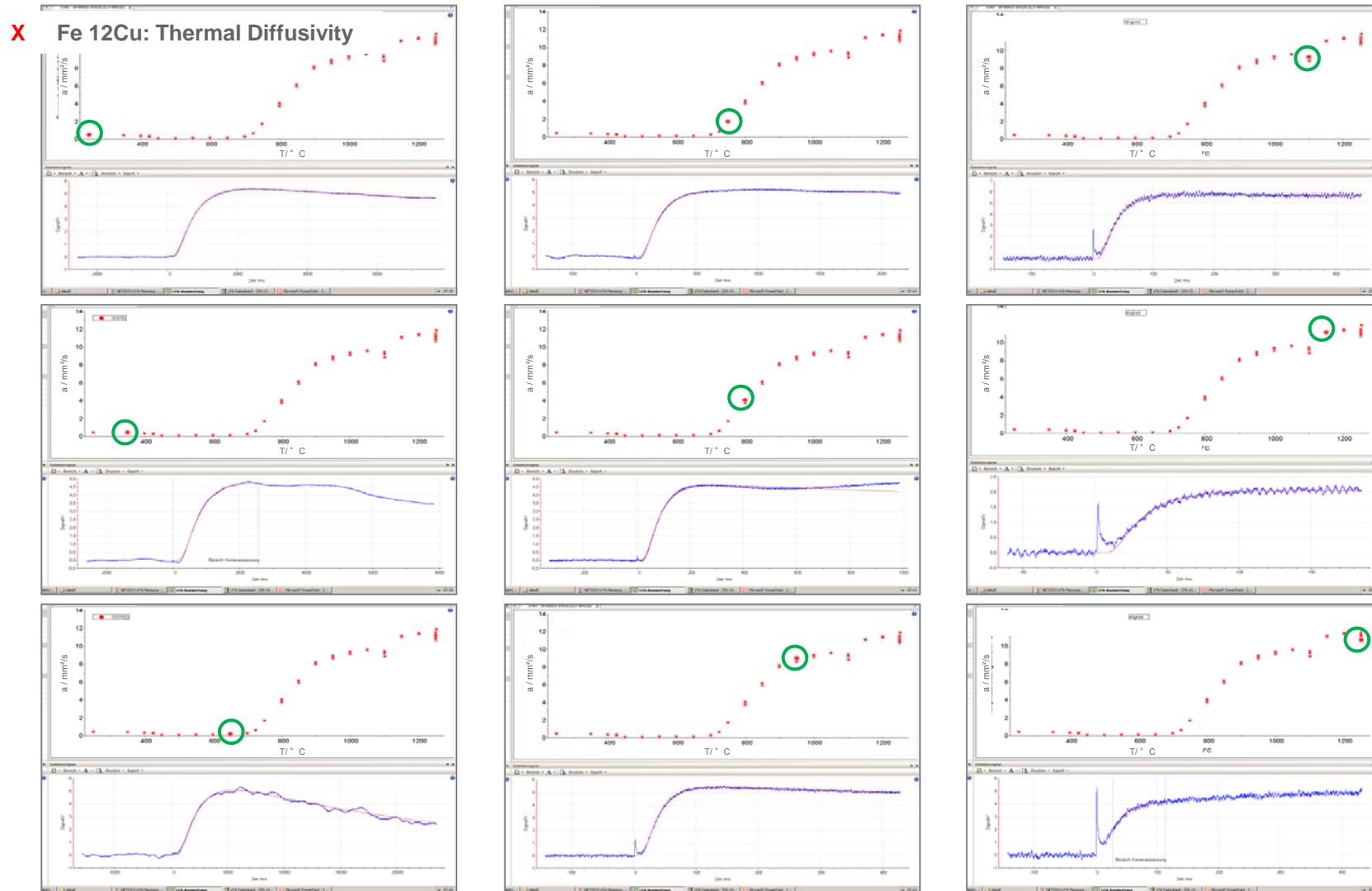
Motivation

... 1D, Adiabatic Boundries, δ - shaped Heat Impact, Series Expansion $O(1)$
... Adiabatic Model – PARKER Interpretation



Motivation

... Experimental Reality: e.g. De-Binding and Sintering of Fe 12Cu



Consequences:

... from these experiences

- Results of a measurement are determined from
 - Sample effects during the measurement
 - **Equipment performance**
 - Examining Model – restrictions, constraints, boundaries ...
- THUS: Uncertainty considerations have to capture
 - Sample related effects
 - **Equipment related effects**
 - **Model related effects**
- How to formulate a sufficient UNCERTAINTY CONCEPT ???
- → ENV 13005 – GUM

GUM's Recommendations *) - Type A

*... Evaluation of standard uncertainty by
statistical analysis of a series of observations*

... Best estimate of the result of the repeated measurement of a quantity Q with n statistically independent observations q_k is the arithmetic mean \bar{q}

$$\bar{q} = \frac{1}{n} \cdot \sum_{k=1}^n q_k$$

... Best estimate of the experimental standard deviation of the underlying probability distribution is the positive square root of the statistic variance $s^2(q_k)$

$$s(q_k) = \sqrt{\frac{1}{n-1} \cdot \sum_{k=1}^n (q_k - \bar{q})^2}$$

... Best estimate of the uncertainty of the arithmetic mean \bar{q} of a series of n independent observations q_k is the positive square root of the experimental standard deviation of the mean

$$u(\bar{q}) = \frac{1}{\sqrt{n}} \cdot s(q_k) := u(x_i)$$

... The standard uncertainty of an output estimate y given from the model function $y = f(x_1, \dots, x_N)$ of N input quantities $\{x_1, \dots, x_N\}$ is calculated from

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

*) ... ENV 13005

GUM's Recommendations *) - Type B

*... Evaluation of standard uncertainty by
scientific judgement - based on all available information*

... 50% chance to measure the estimate x_i of an input quantity X_i within the symmetric intervall $[a_- / a_+]$.

$$u(x_i) = 1,48 a$$

The width of the intervall $[a_- / a_+]$ is $a = (a_- + a_+)/2$.

... 66% chance to measure the estimate x_i of an input quantity X_i within the symmetric intervall $[a_- / a_+]$.

$$u(x_i) = a$$

The width of the intervall $[a_- / a_+]$ is $a = (a_- + a_+)/2$.

... 90% chance to measure the estimate x_i of an input quantity X_i within the intervall $[b_- / b_+]$.
No information about the distribution of the input quantity X_i in $[b_- / b_+]$ available

$$\begin{aligned} u^2(x_i) &= (b_+ - b_-)^2/12 \\ \text{so far } b &= (b_+ - b_-)/2 \\ u^2(x_i) &= b^2/3 \end{aligned}$$

*) ... ENV 13005

EXTENSION of GUM's Recommendations

... Proposal for a Generalized Construction of an Uncertainty Model

- ACCEPT the arithmetic mean
... of a series of independent measurements is the best estimate of any input quantity
- CONSIDER dues to the uncertainty from their causation
 - sample related effects
 - equipment related effects
 - model related effects
- ESTABLISH a construction principle
... to formulate uncertainty models considering equipment and/or model related effects
- ADD ZERO-QUANTITIES C_j to the mean
... as corrections to the arithmetic mean representing effects
... e.g. traceable back to the equipment or to the examining model.
- ATTRIBUTE $u(C_j)$ as the uncertainty of any specific correction C_j

$$q = \frac{1}{m} \cdot \sum_{k=1}^m q_k + \sum C_j \quad C_j = 0 \quad \forall j ; u(C_j) \neq 0$$

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i) + \sum u^2(C_j)$$

Applications

... Laser Flash Method

$$Y = f(X_1, X_2, \dots, X_i, \dots, X_N)$$

$$y = f(q_1, q_2, \dots, q_i, \dots, q_N)$$

$$\bar{q} = \frac{1}{n} \cdot \sum_{k=1}^n q_k$$

$$s(q_k) = \sqrt{\frac{1}{n-1} \cdot \sum_{k=1}^n (q_k - \bar{q})^2}$$

$$u(\bar{q}) = \frac{1}{\sqrt{n}} \cdot s(q_k) := u(x_i)$$

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

$$a(T) = \frac{-\ln(1/4)}{\pi^2} \cdot \frac{h^2}{t_{1/2}}$$

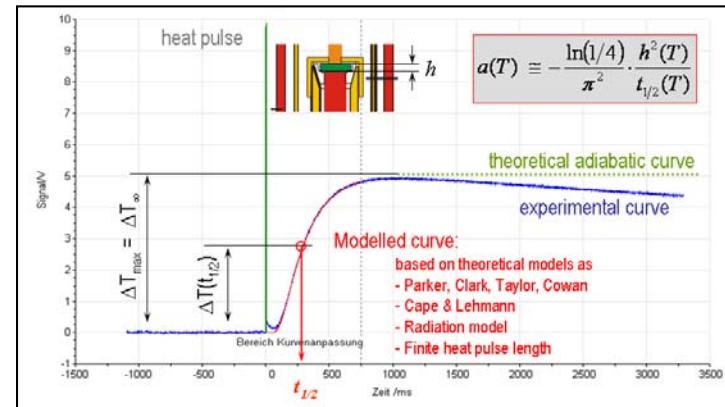
$$a = \frac{1}{n} \cdot \sum_{k=1}^n a_k + \sum_{j=1}^m C_j ; \quad C_j := 0 \forall j$$

$C_s := 0$... Correction from Sample Specific Effects

$C_M := 0$... Correction from Model Specific Effects

$$u_c^2(a) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i) + u^2(C_s) + u^2(C_M)$$

$$u_c^2(a) = ESU^2(a) + SSU^2(a) + MSU^2(a)$$



ESU: Equipment Specific Uncertainty

SSU: Sample Specific Uncertainty

MSU: Model Specific Uncertainty

$$ESU^2(a) = a^2 \cdot \left[\frac{4}{h^2} \cdot u^2(h) - \left(\frac{a \cdot \pi^2}{\ln(1/4) \cdot h^2} \right)^2 \cdot u^2(t_{1/2}) \right]$$

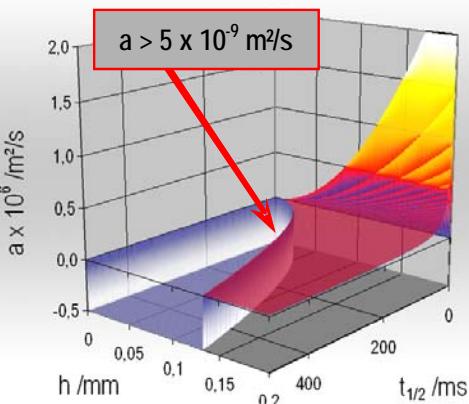
$$SSU^2(a) = s^2(a) = \frac{\sum_{k=1}^n (a_k - \bar{a})^2}{n \cdot (n-1)}$$

MSU²(a) from individual T(t) response

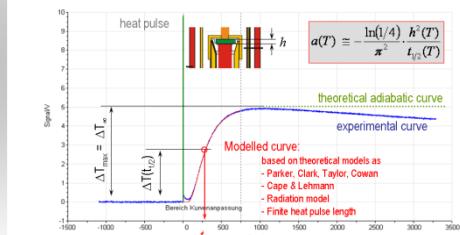
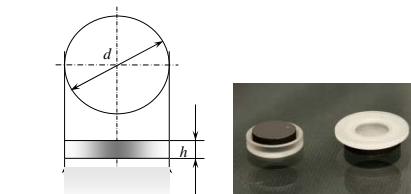
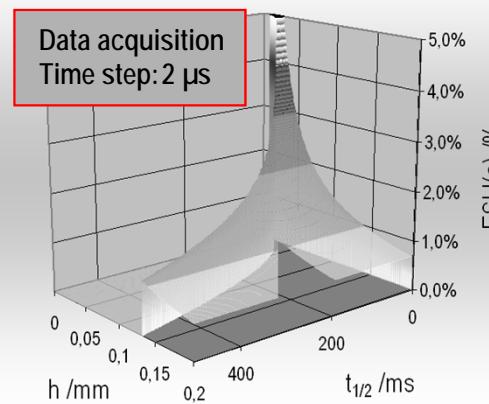
Applications

... *Laser Flash Method: ESU* ^{*}

Thermal Diffusivity: $a(h_s, t_{1/2})$



Relative Equipment Specific Uncertainty: ESU

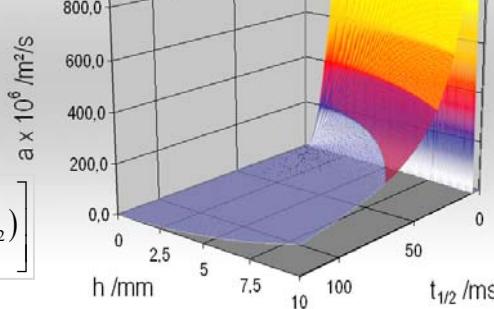


$$a(T) \approx -\frac{\ln(1/4)}{\pi^2} \cdot \frac{h^2(T)}{t_{1/2}(T)}$$

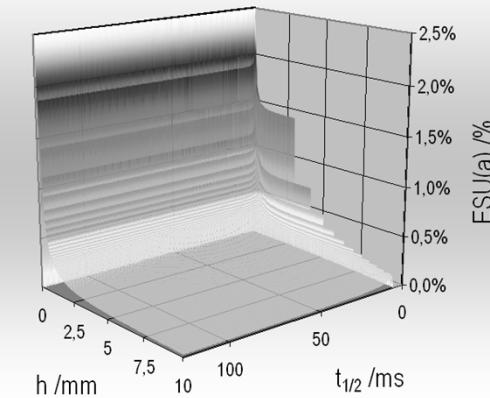
$$h_{min} \approx \sqrt{\frac{\pi^2}{\ln 4} \cdot a \cdot t_{1/2}^{(min)}} \approx 0,06 \cdot \sqrt{a}$$

$$ESU^2(a) = a^2 \cdot \left[\frac{4}{h^2} \cdot u^2(h) - \left(\frac{a \cdot \pi^2}{\ln(1/4) \cdot h^2} \right)^2 \cdot u^2(t_{1/2}) \right]$$

Thermal Diffusivity: $a(h_s, t_{1/2})$



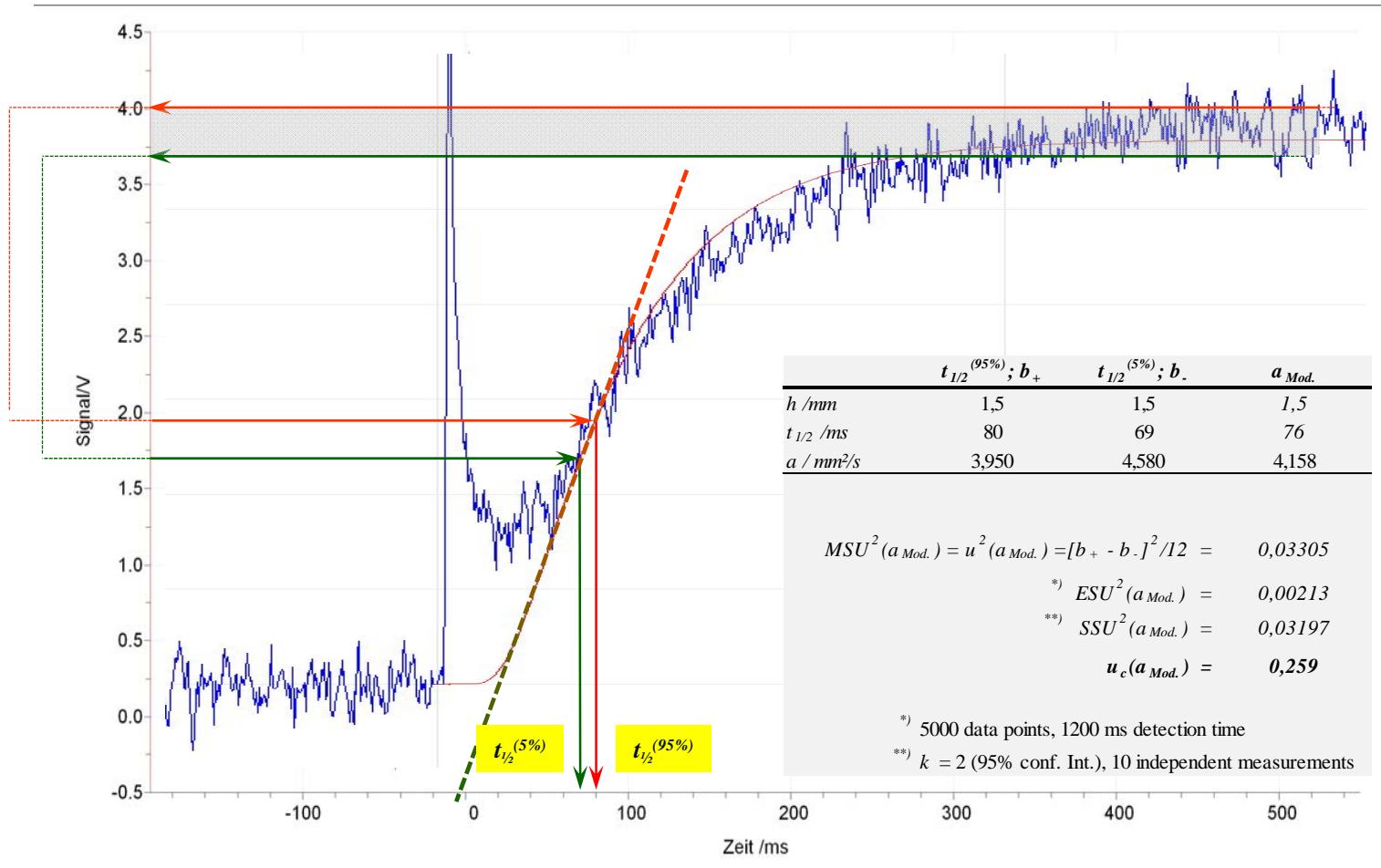
Relative Equipment Specific Uncertainty: ESU



^{*}) ... HERE: NETZSCH® LFA 427

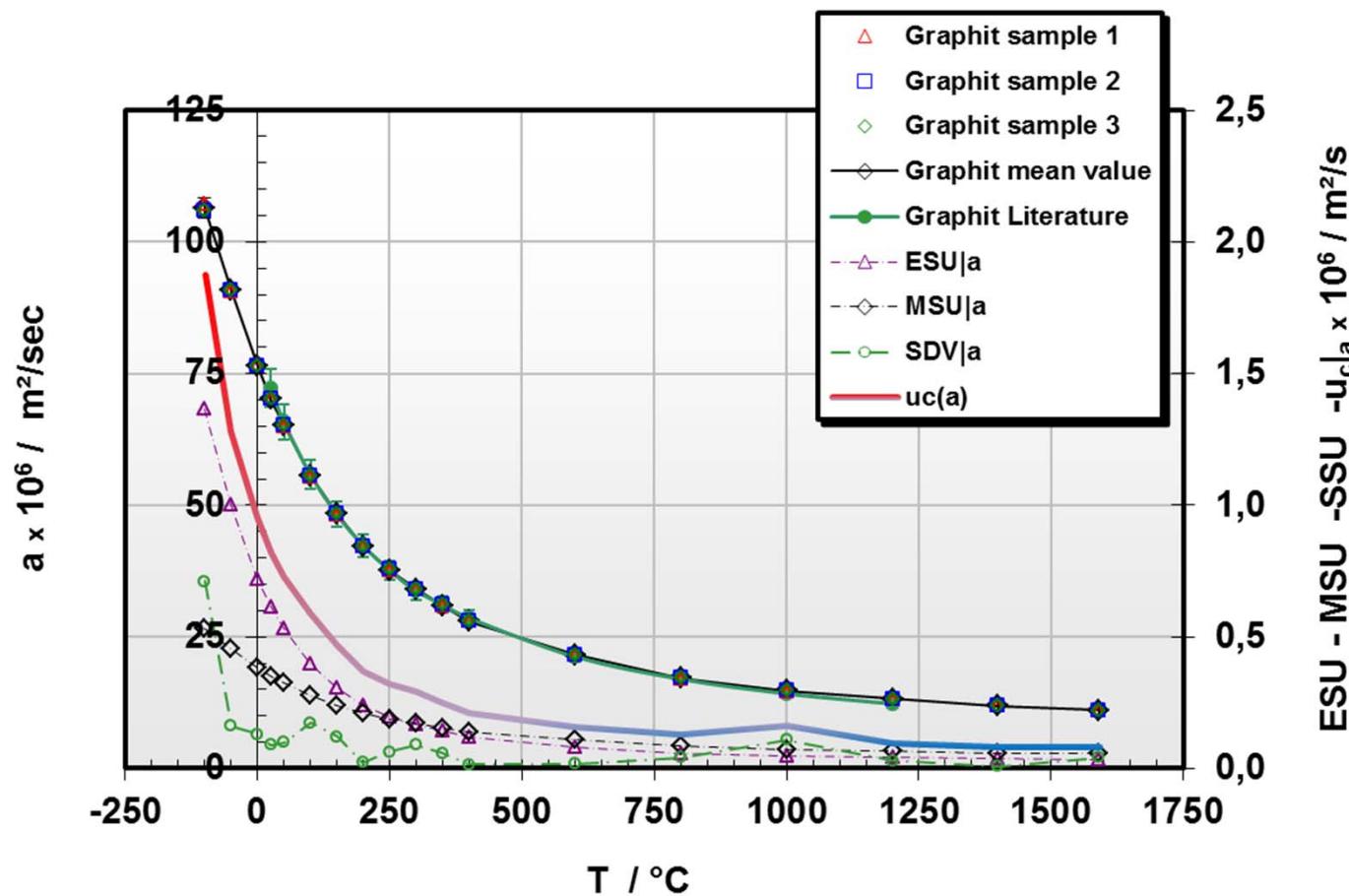
Applications

... *Laser Flash Method: MSU*



Applications

... *Laser Flash Method: $u_c(a)$ from a Graphite reference material*



Applications

... Laser Flash Method: Conclusions

- 2 Zero-quantities C_j are added
 - ... C_E : equipment related
 - ... C_M : model related
- The arithmetic mean
 - ... remains to be the best estimate of the measurement result
- 3 due to the uncertainty from their causation
 - SSU: sample related effects
 - **ESU: equipment related effects**
 - **MSU: model related effects**
- Construction principle
$$u_c^2(a) = \boxed{ESU^2(a) + SSV^2(a) + MSU^2(a)}$$
 - SSU: from standard deviation of a series of measurements
 - **ESU: from equipment performance parameters**
 - **MSU: from specifics of the transient temperature response of each shot**
 - ... is time consuming therefor
 - ... BUT: it cannot be neglected – even NOT in case of optimum measurement conditions
- SSU, ESU, MSU – often do NOT scale from the same magnitude

Applications

... Push Rod Dilatometry

$$Y = f(X_1, X_2, \dots, X_i, \dots, X_N)$$

$$y = f(q_1, q_2, \dots, q_i, \dots, q_N)$$

$$\bar{q} = \frac{1}{n} \cdot \sum_{k=1}^n q_k$$

$$s(q_k) = \sqrt{\frac{1}{n-1} \cdot \sum_{k=1}^n (q_k - \bar{q})^2}$$

$$u(\bar{q}) = \frac{1}{\sqrt{n}} \cdot s(q_k) := u(x_i)$$

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

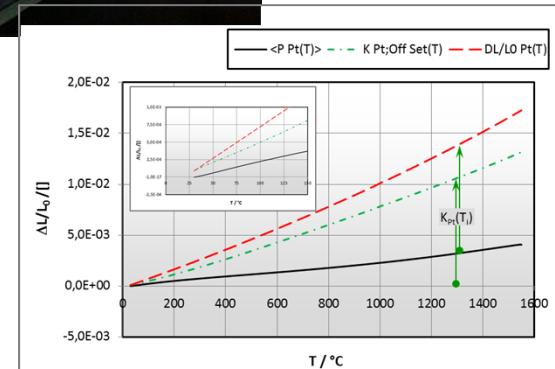
$$K_R(T) = \left(\frac{\Delta L_R(T)}{L_{0;R}} \Big|_{Lit} - \frac{P_R(T)}{L_{0;R}} \right)$$

$$\frac{\Delta L(T)}{L_0} \Big|_S = \frac{P(T)}{L_0} \Big|_S + \frac{K(T)}{L_0} \Big|_R$$

$$\left(\frac{\Delta L/L_0}{CTE} \right) = \frac{1}{n} \cdot \sum_{k=1}^n q_k + \sum_{j=1}^m C_j ; \quad C_j := 0 \forall j$$

$C_S := 0$... Correction from Sample Specific Effects

$C_E := 0$... Correction from Equipment Specific Effects



$$u_c^2 \left(\frac{\Delta L/L_0}{CTE} \right) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i) + u^2(C_S) + u^2(C_E)$$

$$u_c^2(x_i) = MSU^2(x_i) + SSU^2(x_i) + ESU^2(x_i)$$

ESU: Equipment Specific Uncertainty

SSU: Sample Specific Uncertainty

MSU: Model Specific Uncertainty

$$MSU^2 |_{\Delta L/L_0} = u^2 \left(\frac{P_R}{L_{0;R}} \right) + u^2 \left(\frac{\Delta L_R}{L_{0;R}} \Big|_{Lit} \right) = s^2 \left(\frac{P_R}{L_{0;R}} \right) + \left(0,01 \cdot \frac{\Delta L_R}{L_{0;R}} \Big|_{Lit} \right)^2$$

$$SSU^2 |_{\Delta L/L_0} = s^2 \left(\frac{P_S}{L_{0;S}} \right)$$

$$ESU^2 |_{\Delta L/L_0} \cong \left(\frac{10^{-6} / m}{L_{0;i} / m} \right)^2 \cdot \left(\frac{\Delta L(T)}{L_0} \right)^2 \cong (10^{-3})^2 \cdot \left(\frac{\Delta L(T)}{L_0} \right)^2$$

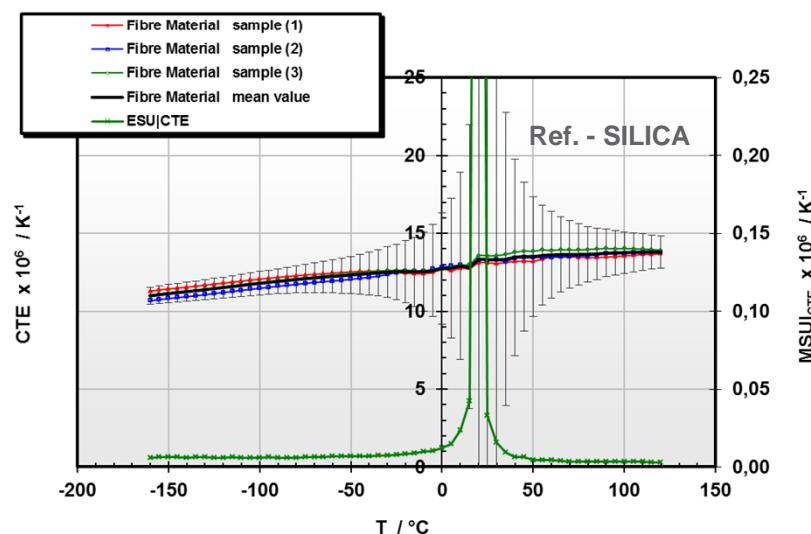
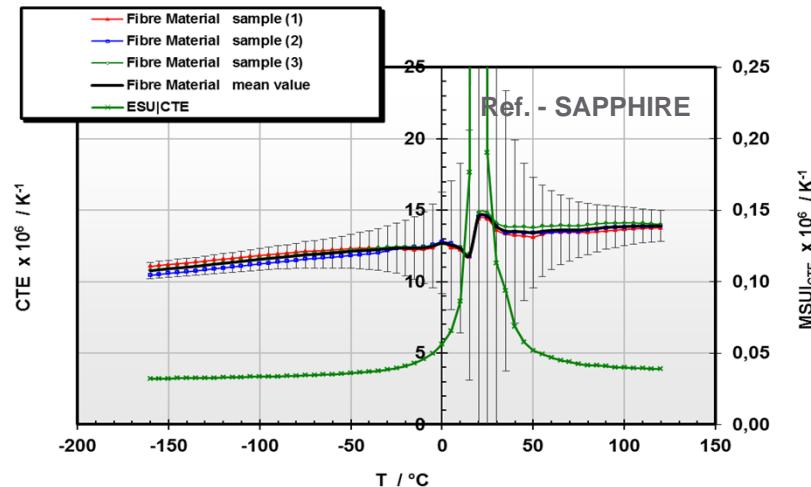
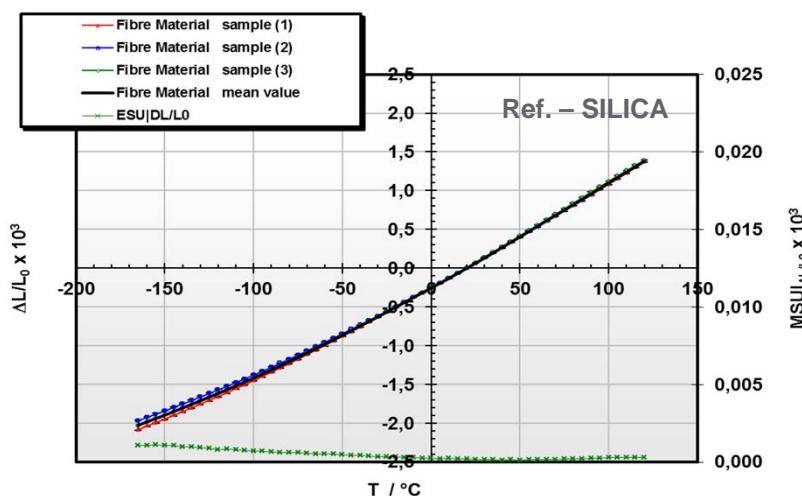
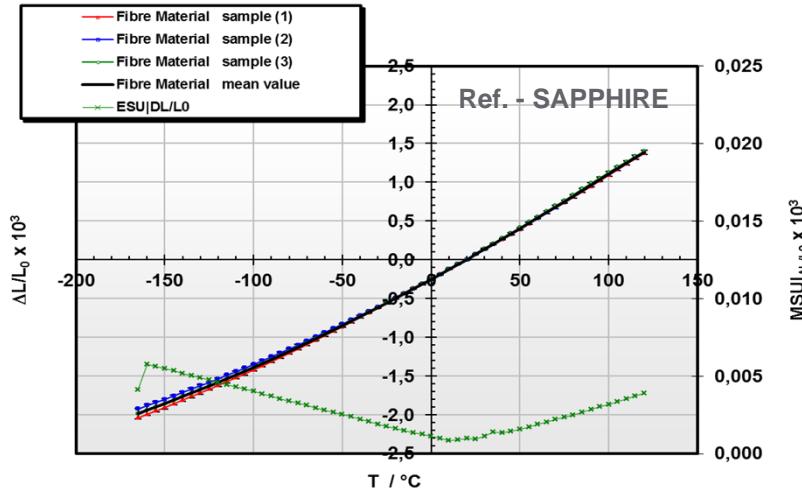
$$MSU^2 |_{CTE} = \frac{1}{\Delta T^2} \cdot MSU^2 \left(\frac{\Delta L_R}{L_{0;R}} \right)$$

$$SSU^2 |_{CTE} = \frac{1}{\Delta T^2} \cdot s^2 \left(\frac{P_S}{L_{0;S}} \right)$$

$$ESU^2 |_{CTE} = \frac{1}{\Delta T^2} \cdot [ESU^2 |_{\Delta L/L_0} + CTE_R^2 \cdot u_c^2(\Delta T)] \cong \frac{1}{\Delta T^2} \cdot [(10^{-3})^2 \cdot CTE_S^2(T) + CTE_R^2(T) \cdot u_c^2(\Delta T)]$$

Applications

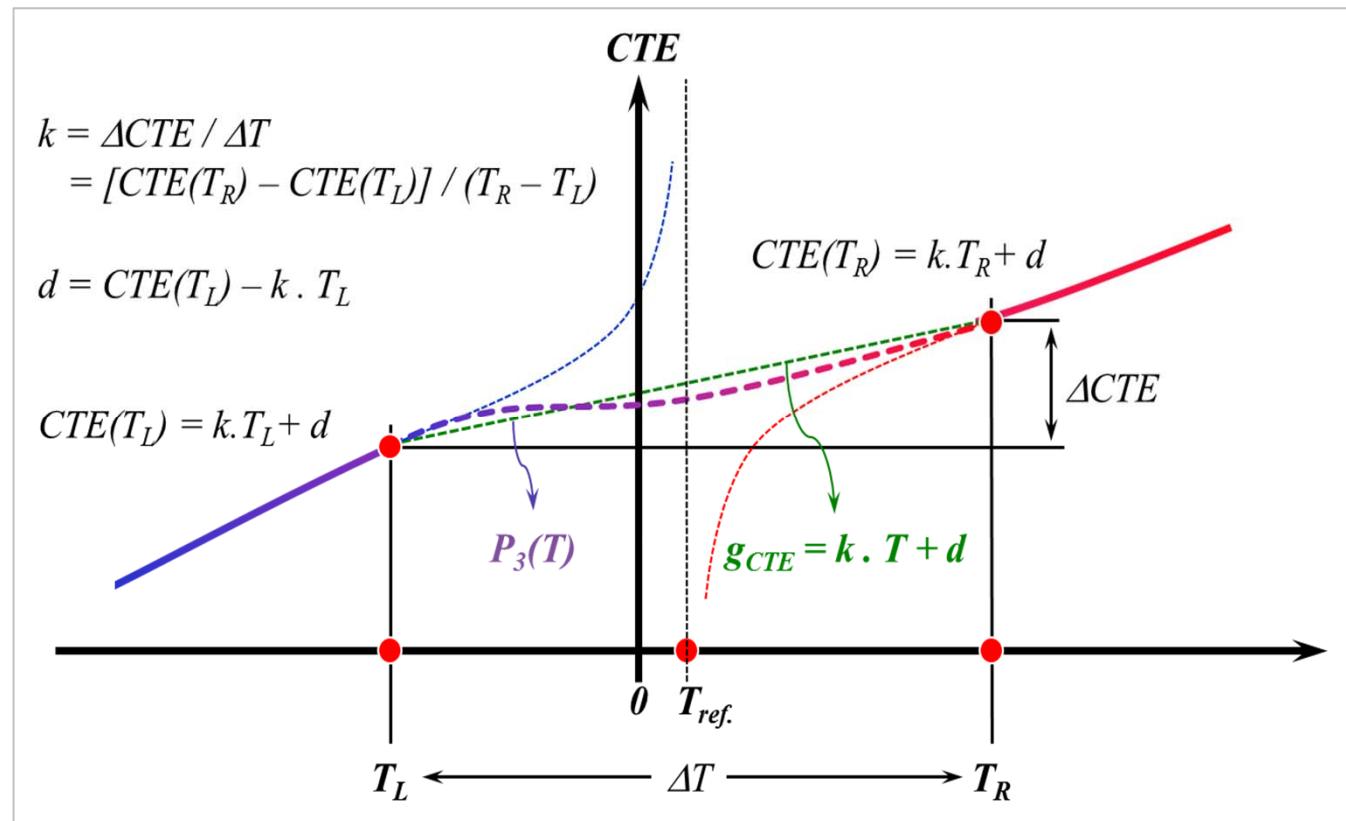
... Push Rod Dilatometry



Applications

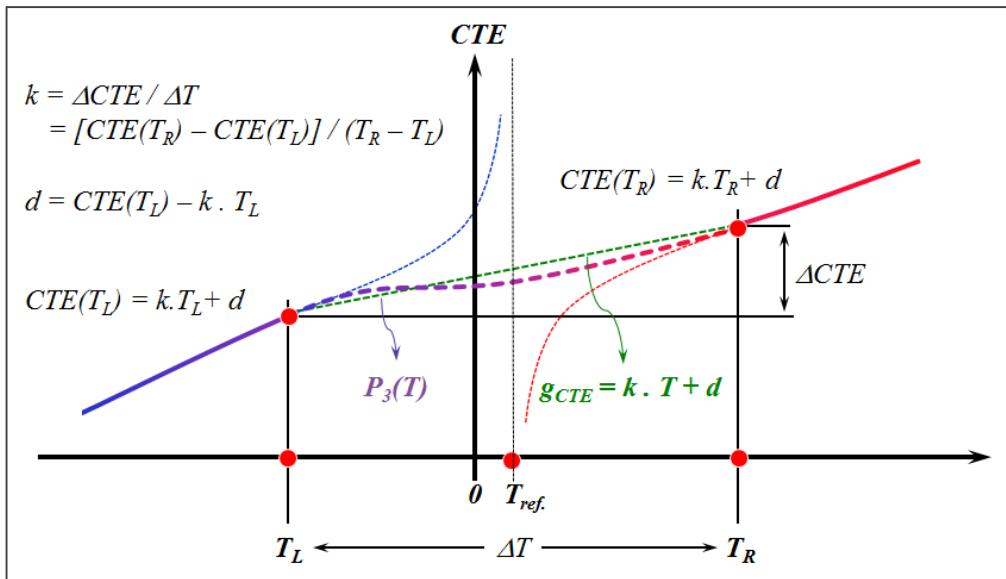
... *Push Rod Dilatometry*

$$u_c^2(P_3(T)) \leq 2 \cdot u_c^2(CTE(T_L))$$



Applications

... Push Rod Dilatometry



$$k = \frac{\Delta CTE}{\Delta T}; \quad d = CTE_L - \frac{CTE_R - CTE_L}{T_R - T_L} \cdot T_L = CTE_L - \frac{\Delta CTE}{\Delta T} \cdot T_L$$

$$g_{CTE}(T) = \frac{\Delta CTE}{\Delta T} \cdot T + CTE_L - \frac{\Delta CTE}{\Delta T} \cdot T_L$$

$$g_{CTE}(T) = \frac{\Delta CTE}{\Delta T} \cdot (T - T_L) + CTE_L$$

Definition 1: $\Delta T = (T_R - T_L)$

Definition 2: $(T - T_L) = \kappa \cdot \Delta T; \quad \kappa \in [0; 1]$

$$g_{CTE}(T) = \kappa \cdot \Delta CTE + CTE_L$$

$$u_C^2(g_{CTE}(T)) = \sum \left(\frac{\partial g_{CTE}(x_i)}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

Variables: $\{x_i\} = \{\Delta CTE; CTE_L\}$

$$u_C^2(g_{CTE}(T)) = \kappa^2 \cdot u^2(\Delta CTE) + 1 \cdot u^2(CTE_L)$$

Assumption: $|T_L| \approx |T_R|$

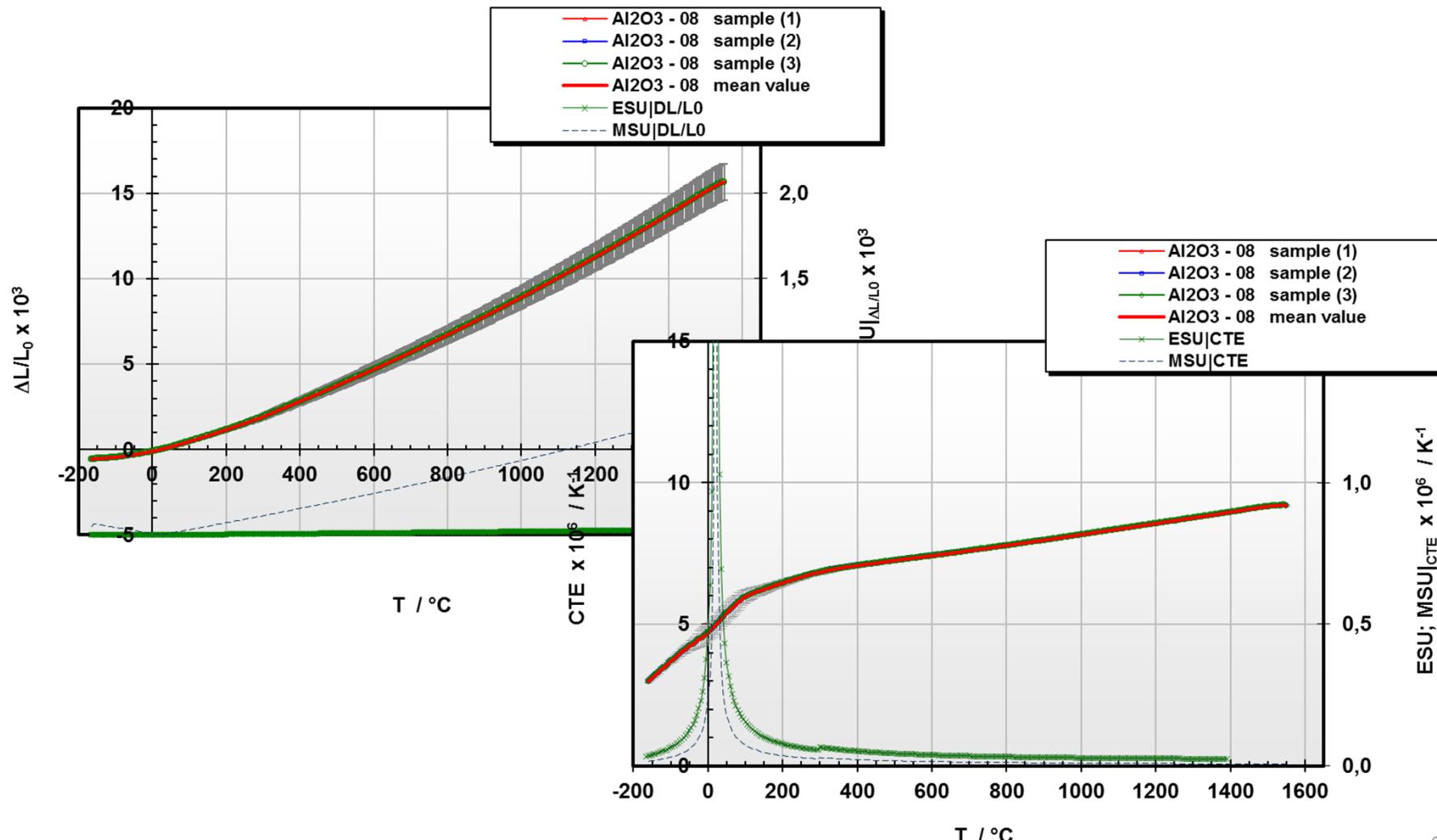
$$u^2(\Delta CTE) \approx u^2(CTE_L) \approx u^2(CTE_R)$$

$$u_C^2(g_{CTE}(T)) \approx (\kappa^2 + 1) \cdot u^2(CTE(T_L))$$

$$u_C^2(g_{CTE}(T)) \leq 2 \cdot u^2(CTE(T_L))$$

Applications

... *Push Rod Dilatometry*



Applications

... Push Rod Dilatometry: Conclusions

- 2 Zero-quantities C_j are added
 - ... C_E : equipment related
 - ... C_S : sample related
- The arithmetic mean
 - ... remains to be the best estimate of the measurement result
- 3 due to the uncertainty from their causation
 - SSU: sample related effects
 - **ESU: equipment related effects**
 - **MSU: model related effects**
- Construction principle
$$u_c^2(x_i) = ESU^2(x_i) + SSV^2(x_i) + MSU^2(x_i)$$
 - SSU: from standard deviation of a series of measurements
 - **ESU: from equipment performance parameters – including thermocouples**
 - ... can casually be neglected – but NOT in case of zero expansion materials
 - **MSU: from specifics of the used reference material – and $K_R(T)$ therefor**
 - ... good choice depends strongly on the optimum consilience on transient thermal histories of reference and sample
- SSU, ESU, MSU – do NOT scale from the same magnitude

Applications

... Dynamic Scanning Calorimetry

$$Y = f(X_1, X_2, \dots, X_i, \dots, X_N)$$

$$y = f(q_1, q_2, \dots, q_i, \dots, q_N)$$

$$\bar{q} = \frac{1}{n} \cdot \sum_{k=1}^n q_k$$

$$s(q_k) = \sqrt{\frac{1}{n-1} \cdot \sum_{k=1}^n (q_k - \bar{q})^2}$$

$$u(\bar{q}) = \frac{1}{\sqrt{n}} \cdot s(q_k) := u(x_i)$$

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i)$$

$$c_p^{(S)}(T) = \left[\frac{DSC^{(S)}(T) - DSC^{(B)}(T)}{DSC^{(R)}(T) - DSC^{(B)}(T)} \right] \cdot \left[\frac{m^{(R)}}{m^{(S)}} \cdot c_p^{(R)}(T) \right] =: [DSC(T)] \cdot [f_E(T)]$$

$$c_p = \frac{1}{n} \cdot \sum_{k=1}^n c_{p;k} + \sum_{j=1}^m C_j ; \quad C_j \doteq 0 \forall j$$

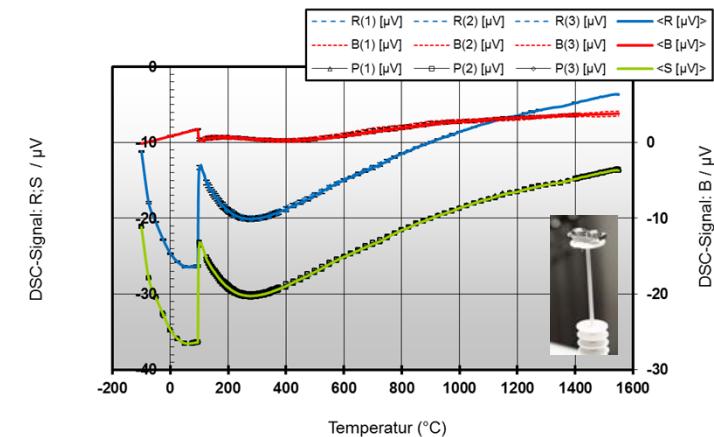
NO Correction needed

IX / 2014 (!)

$$u_c^2(c_p) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 \cdot u^2(x_i)$$



$$u_c^2(c_p) = ESU^2(c_p) + MSV^2(c_p) + SSU^2(c_p)$$



ESU: Equipment Specific Uncertainty

SSU: Sample Specific Uncertainty

MSU: Model Specific Uncertainty

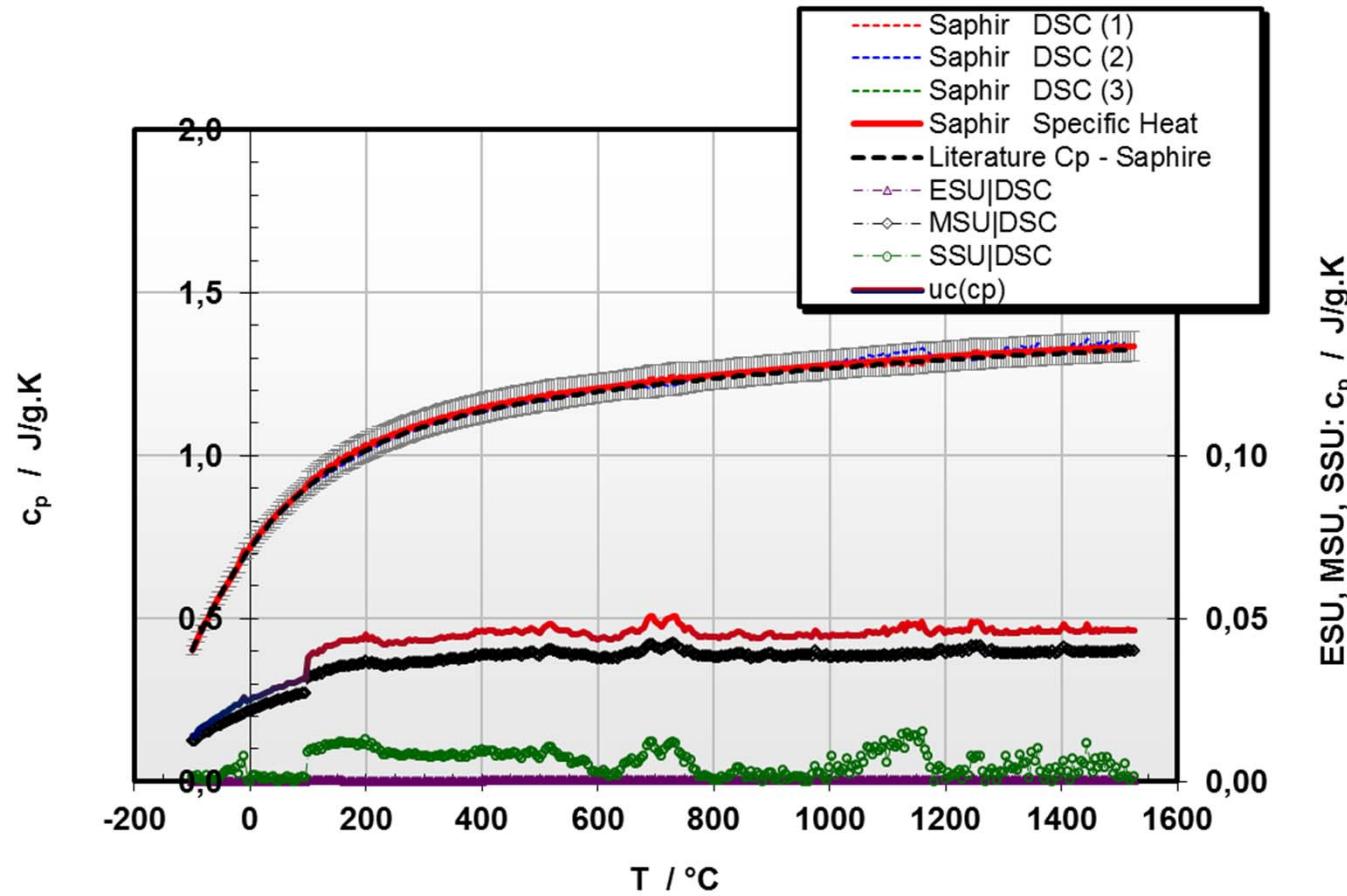
$$ESU^2|_{cp} \equiv f_E^2 \cdot \frac{(DSC^{(S)} - DSC^{(R)})^2}{(DSC^{(R)} - DSC^{(B)})^4} \cdot u^2(DSC^{(B)})$$

$$SSU^2|_{cp} \equiv f_E^2 \cdot \frac{u^2(DSC^{(S)})}{(DSC^{(R)} - DSC^{(B)})^2}$$

$$MSU^2|_{cp} \equiv f_E^2 \cdot \frac{(DSC^{(S)} - DSC^{(B)})^2}{(DSC^{(R)} - DSC^{(B)})^4} \cdot u^2(DSC^{(R)}) + DSC^2(T) \cdot \left(\frac{m^{(R)}}{m^{(S)}} \right)^2 \cdot u^2(c_p^R)$$

Applications

... *Dynamic Scanning Calorimetry*



Applications

... Dynamic Scanning Calorimetry: Conclusions

- The arithmetic mean
... remains to be the best estimate of the measurement result
- 3 due to the uncertainty from their causation
 - SSU: sample related effects
 - **ESU: equipment related effects**
 - **MSU: model related effects**
- Construction principle
$$u_c^2(c_p) = ESU^2(c_p) + SSV^2(c_p) + MSU^2(c_p)$$
 - SSU: from standard deviation of a series of sample measurements
 - **ESU: from standard deviation of a series of empty measurements**
... can casually be neglected – but performance is mapped to measurements of references and samples
 - **MSU: from specifics of the used reference material – and $c_p(T)$ therefor**
... main contribution to the standard uncertainty $u_c(c_p)$ – because of uncertainty of reference data
 - **THUS:** the derived uncertainty model does NOT require to add zero-quantities C_j
 - **BUT:** in more complex models this might be different
- SSU, ESU, MSU – do NOT scale from the same magnitude

Summary

Proposal to Reduce GUM's Recommendations to Practice in Standard Methods of Thermophysics

- Using *GUM / ENV 13005* – Uncertainty Models are constructed for
 - Laser Flash
 - Push Rod Dilatometry
 - Dynamic Scanning Calorimetry
 - Hot Wire Method
 - Heat Flow Meter
 - Comparative Method
- Construction Principle
 - Dues to the uncertainty from their causation are implemented
 - *ESU*: equipment related effects
 - *MSU*: model related effects
 - *SSU*: sample related effects
 - The arithmetic mean
 - ... Remains to be the best estimate of the measurement result
 - ... Zero-quantities C_j necessary to be added
 - ... $u(C_j)$ are attributed to *ESU / MSU*
 - Effects from calibrations to be implemented (T-Calib. S-Calib, ...)
- Best Practice Recommendations from Uncertainty Analysis

$$u_c^2(a) = ESU^2(a) + SSV^2(a) + MSU^2(a)$$

Structure of Contributions: Special Issue HTHP

To Reduce GUM's Recommendations to Practice in <METHOD>

- Introduction
 - ... deducing <METHOD> from basic concepts of thermodynamics
- Experimental Description of <METHOD>
 - ... Experimental Requirements
- Theory to <METHOD>
 - ... including constraints and boundaries
- Uncertainty Concept
 - ... based on Theory to <METHOD>
 - ... referring to calibration needs (e.g. T-calibration)
 - ... FINALLY: dues attributed to: **ESU**, **MSU**, **SSU**
 - ... discussion of the uncertainty concept and conclusions thereof → referring to “Examples” (see downwards)
- Hints to “Good Laboratory Practice” for <METHOD>
 - ... derived from uncertainty concept
- Examples
 - Analysis of Measurement Results from a Reference Material
 - Analysis of Measurement Results from a Material
 - ... which fits to basic constraints and boundaries of <METHOD>
 - Analysis of Measurement Results from a Material
 - ... which does not fully fit to basic constraints and boundaries of <METHOD>
 - Figures should explicitly show **ESU**, **MSU**, **SSU**
- Summary

Contributions

*To Reduce GUM's Recommendations to Practice
in Standard Methods of Thermophysics*

8	Contributions	Special Emphasis to ...
Hohenauer		
1	Introduction & Concept	Concept to construct uncertainty models
Blumm, Hohenauer, Moukhina		
1	Dilatometry	Equipment specific uncertainty in push rod dilatometry
Hemberger, Mehling		
1	DSC	Main contribution to combined standard uncertainty in Dynamic Scanning Calorimetry DSC
Moukhina, Blumm, ...		
1	Laser Flash	Model specific uncertainty of diffusivity data from FLASH DEVICES
Rohde		
1	Thermal Reflectance	Main contribution to combined standard uncertainty in ALTERNATIVE FLASH CONCEPTS
Ebert, ...		
1	Heat Flow Meter	Equipment specific and model specific contributions to standard uncertainty in heat flow meters
1	Hot Wire Method	Equipment specific and model specific contributions to standard uncertainty in hot wire devices
Kaschnitz		
1	Cmparative Method	Equipment specific and model specific contributions to standard uncertainty in comparative devices