Uncertainty Analysis for Heat-flux DSC Measurements

EMRP
European Metrology Research Programme
Programme of EURAMET

Power
Plant
Metrology

EMRP

(European Metrology Research Programme)

- metrology-focused
- coordinated R&D
- integration of national research programmes
- supported by the European Commission
- collaboration between National Measurement Institutes
- reducing duplication and increasing impact
- managed by EURAMET

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EURAMET
European Association of National Metrology Institutes

EMRP Call 2009 – Energy

Joint Research Projects (JRPs)

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Number	Short Name	Full Name	JRP Coordinator
ENG01	GAS	Characterisation of Energy Gases	Dr Dai Jones (NPL)
ENG02	Harvesting	Metrology for Energy Harvesting	Dr Jürgen Melcher (PTB)
ENG03	LNG	Metrology for Liquefied Natural Gas	Ir Oswin Kerkhof (VSL)
ENG04	SmartGrid	Metrology for Smart Electrical Grids	Dr Gert Rietveld (VSL)
ENG05	Lighting	Metrology for Solid State Lighting	Dr Marijn van Veghel (VSL)
ENG06	Powerplants	Metrology for Improved Power Plant Efficiency	Dr Thomas Lederer (PTB)
ENG07	HVDC	Metrology for High Voltage Direct Current	Dr Anders Bergman (SP)
ENG08	MetroFission	Metrology for New Generation Nuclear Power Plants	Dr Lena Johansson (NPL)
ENG09	Biofuels	Metrology for Biofuels	Dr Paola Fisicaro (LNE)

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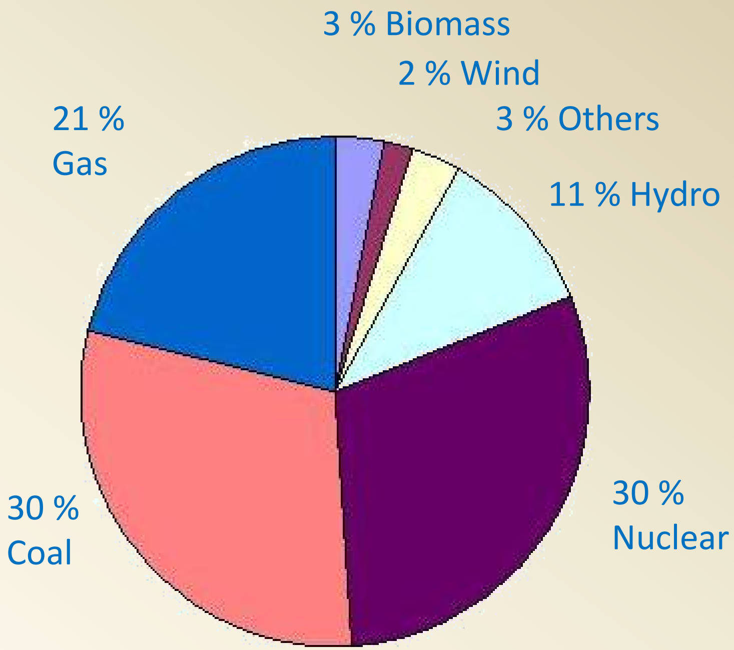
ENG06

Improved Power Plant Efficiency

Optimized steering processes and safe extensions of process conditions by;

- metrological research to **substantially reduce the measurement uncertainty** of the most important control parameters in situ:
    - Temperature
    - Flow
    - Thermal energy
    - Electrical output
- **research on advanced materials** needed in future turbines



Electricity generation by fuel used in power plants, EU-27, 2006

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Project partners

- PTB, Germany (coordination)
- NPL, United Kingdom
- LNE, France
- SP, Sweden
- VSL, The Netherlands
- MIKES, Finland
- CMI, Czech Republic
- BEV, Austria
- TUG, Austria
- DTI, Denmark

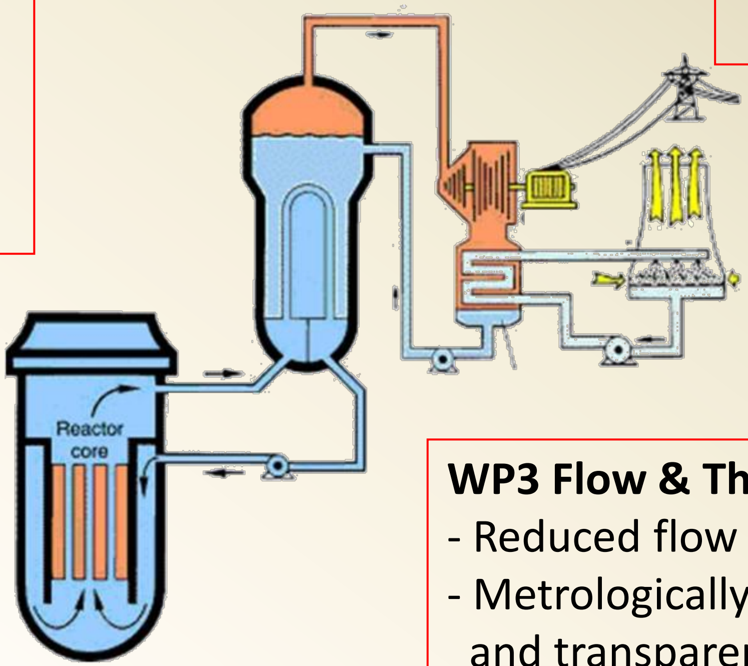
Advisory partners

Rolls-Royce
VATTENFALL
KROHNE
EUROHEAT & POWER
AREVA
e·on
VGB
DONCASTERS
Strålsäkerhetsmyndigheten
Swedish Radiation Safety Authority
Endress+Hauser
People for Process Automation
ZPA NOVÁ PAKA
Westinghouse
TÜVRheinland®
Genau. Richtig.

Project overview

WP1 - Temperature
- Contact thermometry up to 700 °C
- Radiation thermometry up to 1500 °C

WP4 - Electricity
- Fast, and accurate (traceable) on-site measurements



WP2 - Thermophysical properties
- Characterization of high temperature thermal properties
- Determine emissivity values

WP3 Flow & Thermal Energy
- Reduced flow meter uncertainty
- Metrologically accepted and transparent models for "calibration extrapolation"
- Temperature mapping in pipelines

WP 2 – Thermophysical properties

Scientific and technological objectives

Develop accurate facilities for the measurement of thermal properties of homogeneous solid materials and thermal barrier coatings up to 1500°C

Perform thermophysical properties measurements of on Ni-base alloys and TBCs specimens under temperature conditions encountered in gas turbines

Thermal diffusivity a ($m^2 \cdot s^{-1}$)	**Emissivity** ε
Specific heat c_p ($J \cdot kg^{-1} \cdot K^{-1}$)	**Thermal expansion** α (K^{-1})

WP 2 – Thermophysical properties

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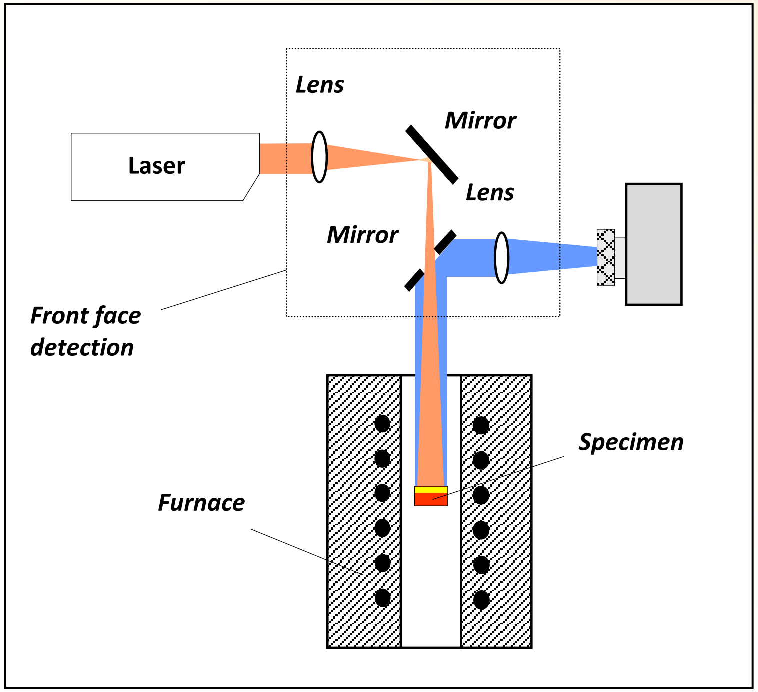
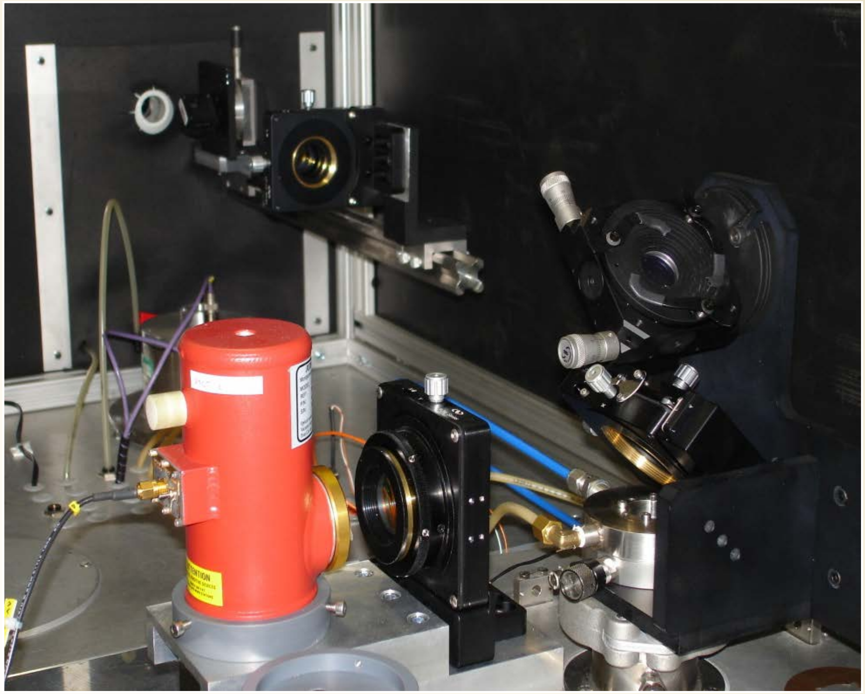
Implementation of a metrological setup for the measurement of thermal diffusivity of multilayered systems up to 1500°C

- Measurements of thermal diffusivity by “front face laser flash” method
- Design and assembly of a “front-face detection” system on the existing diffusivimeter of LNE





WP 2 – Thermophysical properties

Development of reference metrological facilities for the measurement of emissivity of solid materials up to 1500 °C

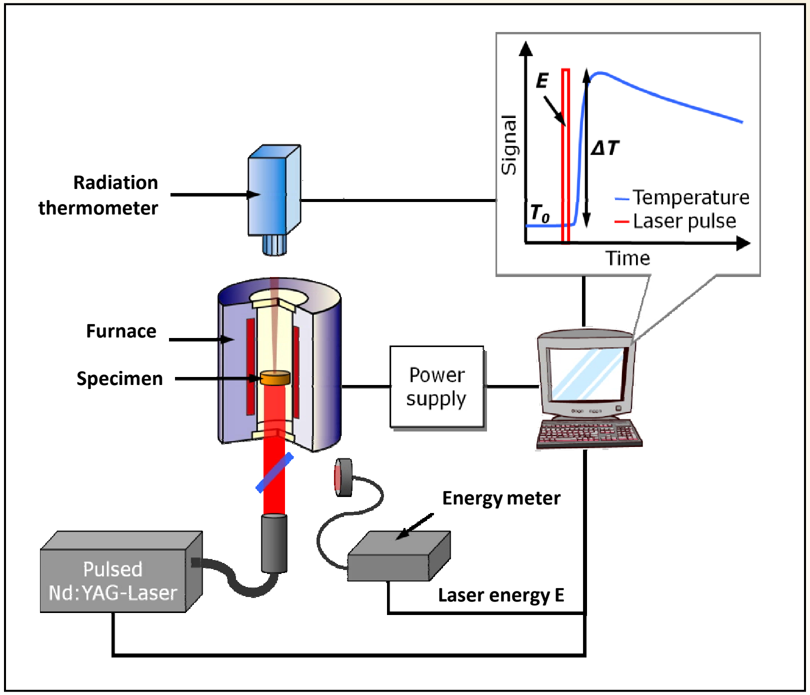
- Two complementary facilities based on different metrological approaches

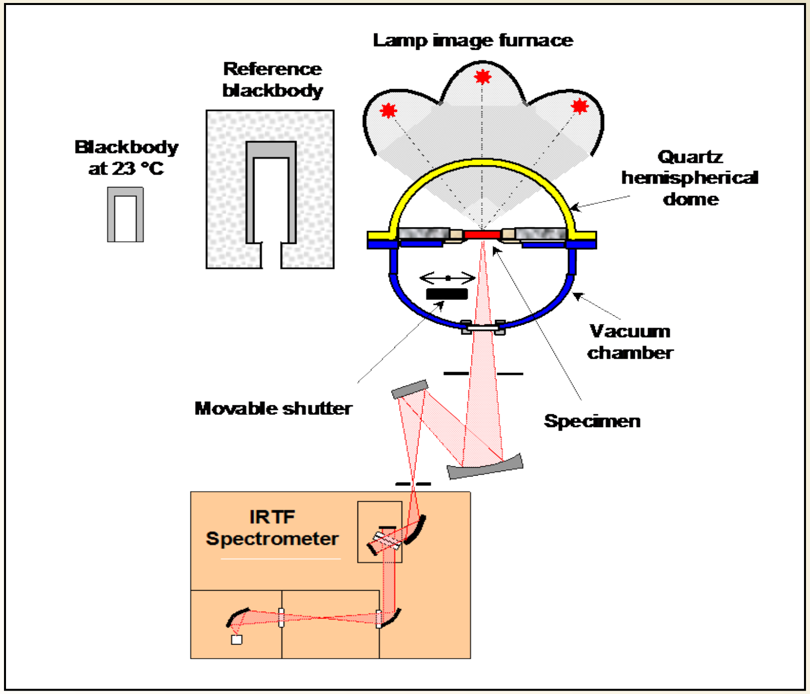
Calorimetric method

$$\varepsilon_\lambda^{\perp}(T)\cdot E_\lambda = m\cdot c_p(T)\cdot \Delta T$$

Optical method

$$\varepsilon'_\lambda(T) = \ell_\lambda(T)/\ell^{\circ}_\lambda(T)$$





WP 2 – Thermophysical properties

Study of specific heat and thermal expansion measurements of TBC and Ni-base alloys at high temperature (up to 1500°C)

- Study of the effects of oxygen on the specific heat measurement
- Comparison of X-ray measurements of TBCs against dilatometer meas.
- Relation between thermal expansion and microstructure for Ni-base alloys

$$\lambda = a \cdot \rho \cdot c_p$$

- Assessment of thermal conductivity by indirect approach

Specific heat capacity at high temperature

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- Common practice for uncertainty?

- Literature?

- Need for more?

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Available Equipment

Commercial Heat Flux DSCs

- TUG
  - DSC with Platinum furnace, up to 1500°C
  - STA (combination of TGA/DSC), up to 1500°C

- PTB
  - DSC with Platinum furnace, up to 1500°C
  - DSC with Tungsten furnace, up to 2400°C

Heat-flux DSC
Working Equation

$$c_{p,s} = \frac{m_{cal} \cdot c_{p,cal}}{m_s} \cdot \frac{S_s - S_0}{S_{cal} - S_0}$$

c_p	… Specific heat capacity	s	… Sample
m	… Mass	cal	… Calibration sample
S	… Signal (heat flow rate)	0	… Empty

Uncertainty contributions

- Measurands from working equation $(m_s,\ m_{cal}, c_{p,cal}, S_{cal}, S_s, S_0)$

- Reproducability, Repeatability
  - Instrument specifications (e.g.: S/N-ratio)
  - Operator
    - Handling and positioning of crucibles and samples
  - Heating rate
  - Sample material

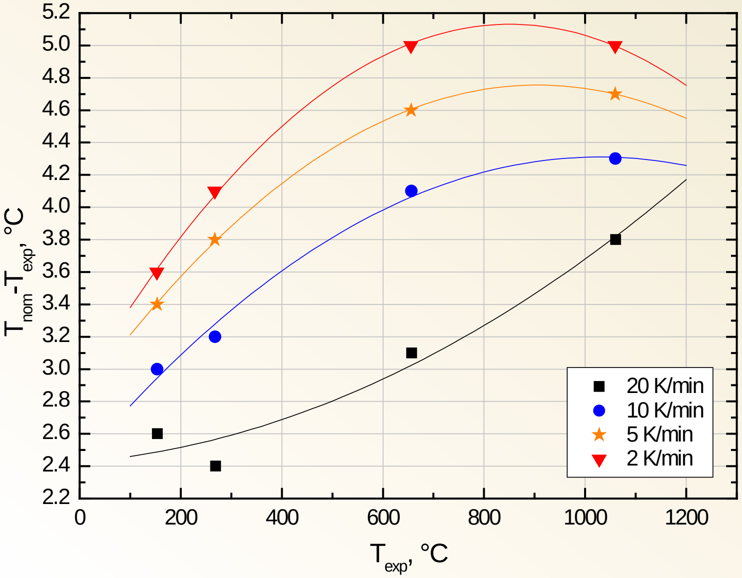
- Temperature
  - Calibration
    - Melting point of reference material
    - Heating rate, for extrapolation to 0 K/min
    - Thermal lag

- Heat flow calibration

Calibration

Temperature

- Temperature
  - Calibration
    - Melting point of reference material
      e.g.: metals - In, Sn, Pb, Zn, Al, Ag, Au, Ni



Literature:

- IUPAC Technical Report: Standards, Calibration, and Guidelines in Microcalorimetry, Part 2. Calibration Standards For Differential Scanning Calorimetry, Pure Appl. Chem., Vol. 78, No. 7, pp. 1455-1476, 2006

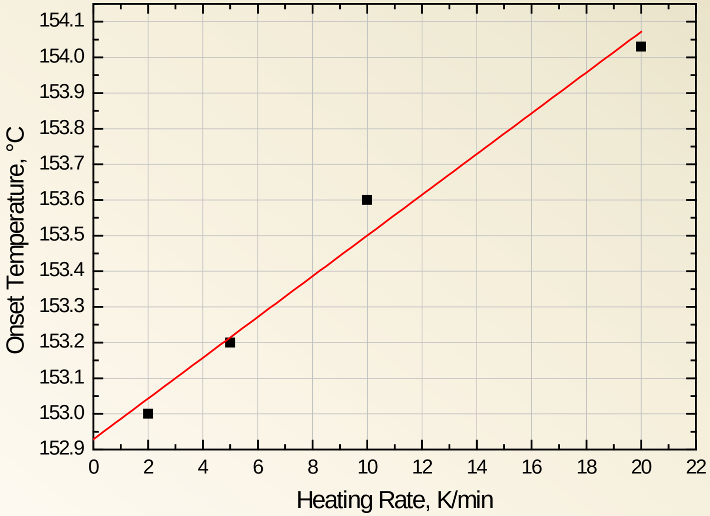
GEFTA –Recommendations:

- The caloric calibration of scanning calorimeters, Thermochim. Acta 247, 129-168, 1994

Calibration

Temperature

- Temperature
  - Calibration
    - Melting point of reference material
      e.g.: metals - In, Sn, Pb, Zn, Al, Ag, Au, Ni
    - Heating rate, for extrapolation to 0 K/min
      -> steady-state conditions



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Calibration

Temperature

- ▶ Temperature
  - o Calibration
    - – Melting point of reference material
      e.g.: metals - In, Sn, Pb, Zn, Al, Ag, Au, Ni
    - – Heating rate, for extrapolation to 0 K/min
      -> steady-state conditions
    - – Thermal lag – sample temperature lag
      depends on thermal coupling, heat capacity of sample, heating-/ cooling-rate

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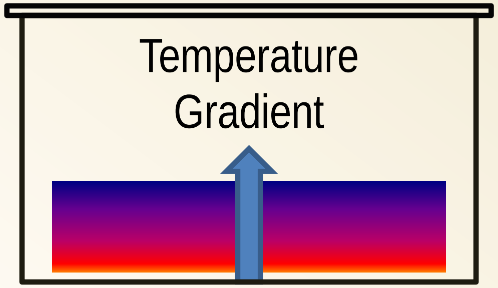
Calibration



Difference to mean sample temperature:

$$\Delta T = \frac{C_p \rho}{3\lambda} \beta d^2$$

Heat flow rate

- By means of a known heat capacity
- Uncertainty due to mass dependency

Budget-Contributions

m_{cal}

$c_{p,cal}$

S_{cal}

ΔS_{cal}

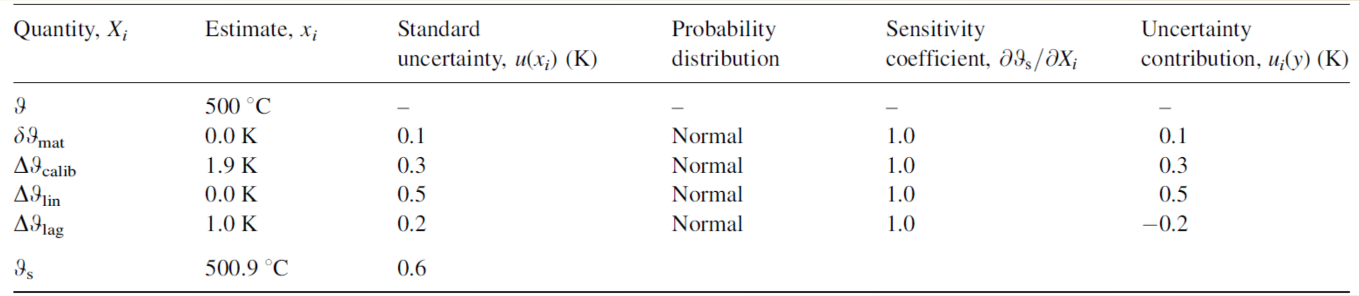
m_s

S_s

ΔS_s

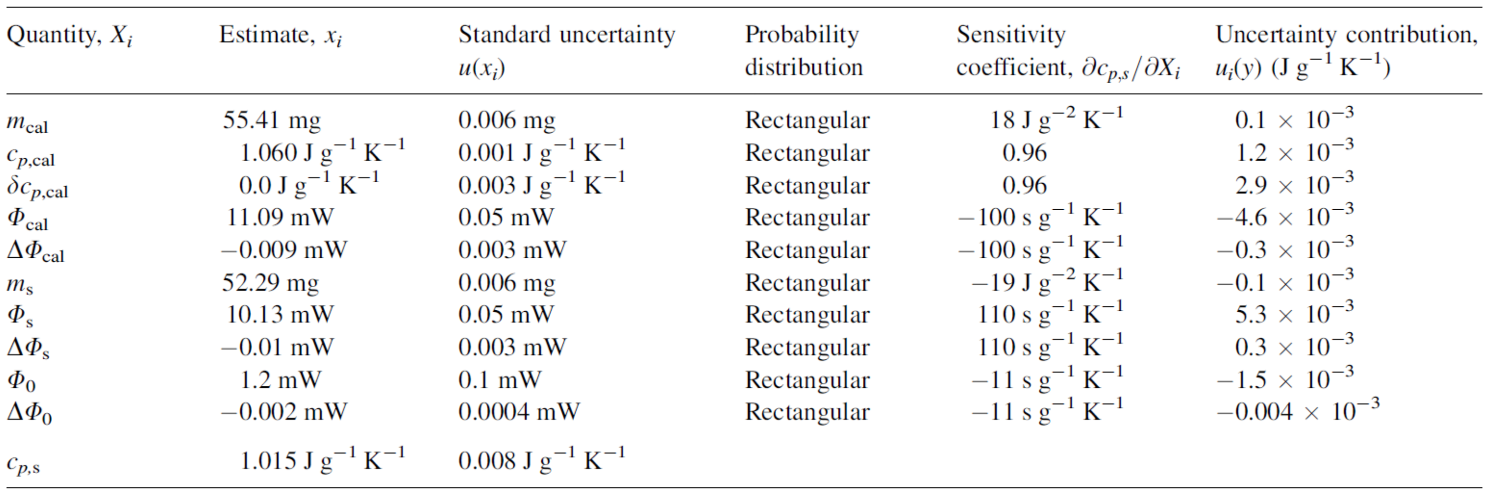
S_0

ΔS_0



Quantity, X_i	Estimate, x_i	Standard uncertainty, $u(x_i)$ (K)	Probability distribution	Sensitivity coefficient, $\partial\vartheta_s/\partial X_i$	Uncertainty contribution, $u_i(y)$ (K)
ϑ	500 °C	–	–	–	–
$\delta\vartheta_{mat}$	0.0 K	0.1	Normal	1.0	0.1
$\Delta\vartheta_{calib}$	1.9 K	0.3	Normal	1.0	0.3
$\Delta\vartheta_{lin}$	0.0 K	0.5	Normal	1.0	0.5
$\Delta\vartheta_{lag}$	1.0 K	0.2	Normal	1.0	−0.2
ϑ_s	500.9 °C	0.6			

T=250°C



Quantity, X_i	Estimate, x_i	Standard uncertainty $u(x_i)$	Probability distribution	Sensitivity coefficient, $\partial c_{p,s}/\partial X_i$	Uncertainty contribution, $u_i(y)$ (J g^{-1} K^{-1})
m_{cal}	55.41 mg	0.006 mg	Rectangular	18 J g^{-2} K^{-1}	0.1×10^{-3}
$c_{p,cal}$	1.060 J g^{-1} K^{-1}	0.001 J g^{-1} K^{-1}	Rectangular	0.96	1.2×10^{-3}
$\delta c_{p,cal}$	0.0 J g^{-1} K^{-1}	0.003 J g^{-1} K^{-1}	Rectangular	0.96	2.9×10^{-3}
Φ_{cal}	11.09 mW	0.05 mW	Rectangular	−100 s g^{-1} K^{-1}	-4.6×10^{-3}
$\Delta\Phi_{cal}$	−0.009 mW	0.003 mW	Rectangular	−100 s g^{-1} K^{-1}	-0.3×10^{-3}
m_s	52.29 mg	0.006 mg	Rectangular	−19 J g^{-2} K^{-1}	-0.1×10^{-3}
Φ_s	10.13 mW	0.05 mW	Rectangular	110 s g^{-1} K^{-1}	5.3×10^{-3}
$\Delta\Phi_s$	−0.01 mW	0.003 mW	Rectangular	110 s g^{-1} K^{-1}	0.3×10^{-3}
Φ_0	1.2 mW	0.1 mW	Rectangular	−11 s g^{-1} K^{-1}	-1.5×10^{-3}
$\Delta\Phi_0$	−0.002 mW	0.0004 mW	Rectangular	−11 s g^{-1} K^{-1}	-0.004×10^{-3}
$c_{p,s}$	1.015 J g^{-1} K^{-1}	0.008 J g^{-1} K^{-1}			

S. Rudtsch, Thermochimica Acta 382, pp 17-25, 2002

Literature:
Uncertainty for High Temp. DSC

- $T > 800$°C