Anton Paar

NON-AMBIENT XRD

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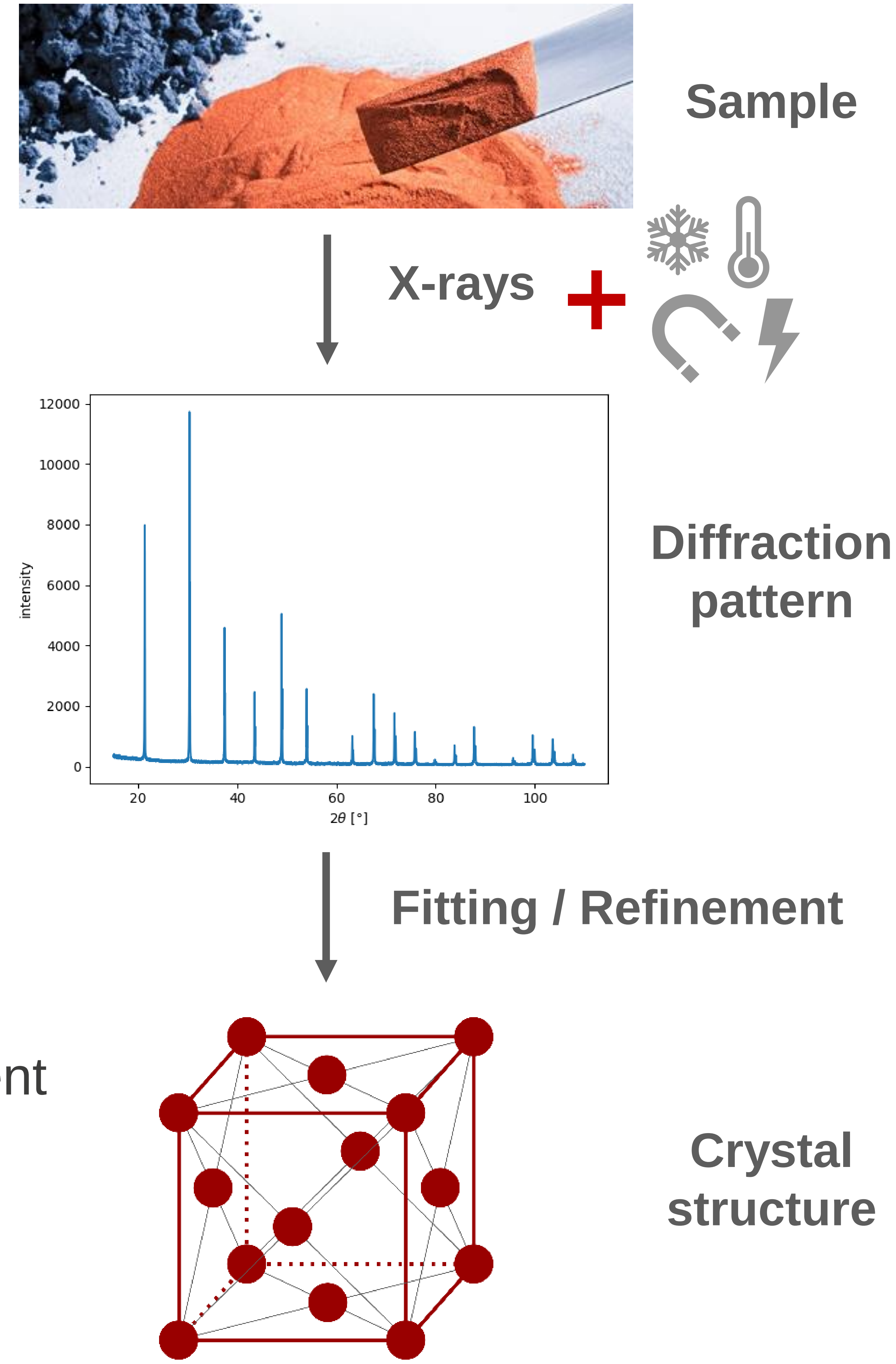
NON-AMBIENT X-RAY DIFFRACTION (NA-XRD)

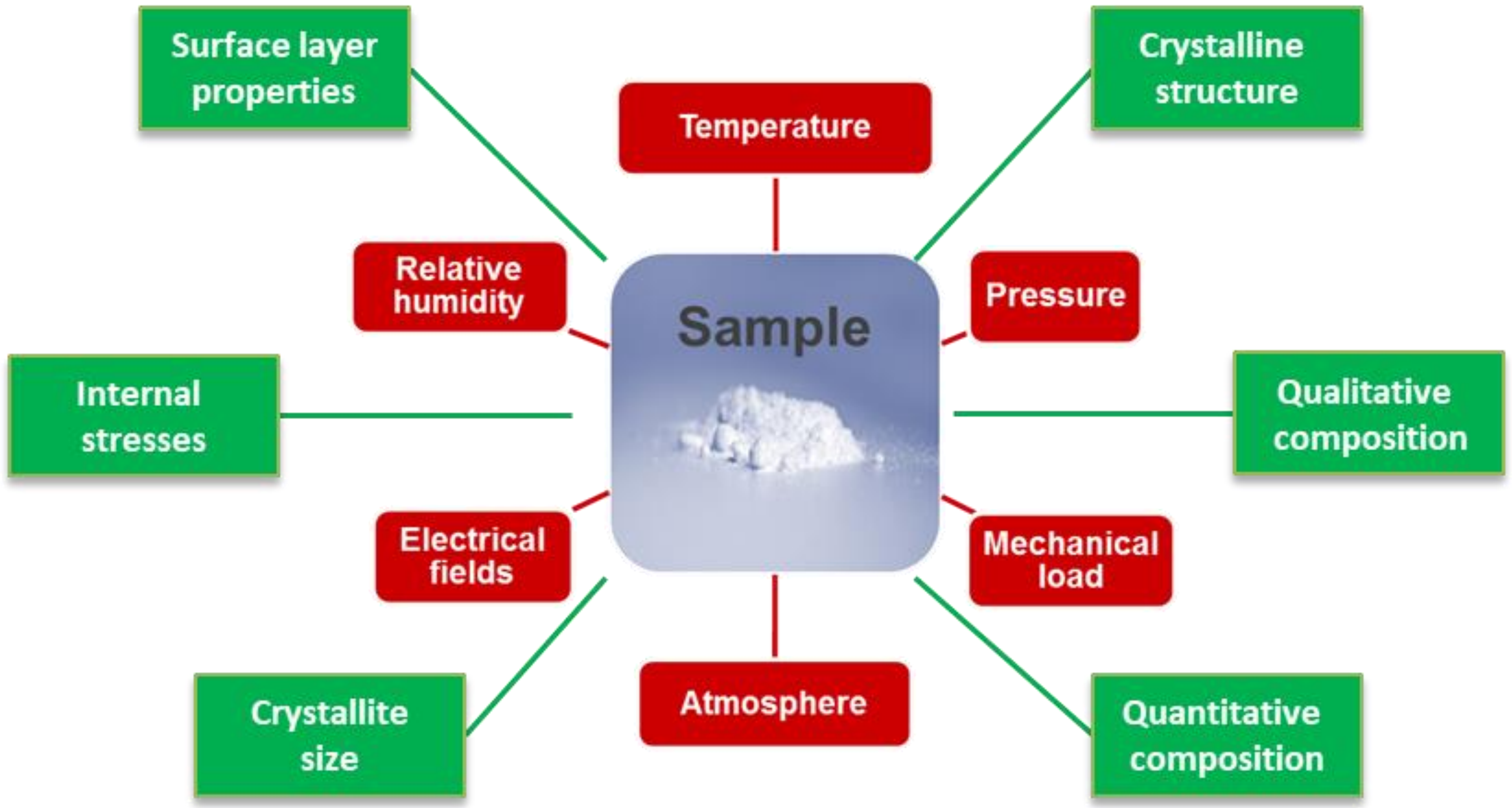
BASICS OF NA-XRD

WHAT IS DIFFERENT BETWEEN XRD UNDER AMBIENT AND NON-AMBIENT CONDITIONS?

- Parameters such as temperature, pressure, humidity, atmosphere, are varied during the measurement
- Non-ambient XRD attachment is needed, but otherwise measurement set up and XRD theory remains the same
- Some additional aspects must be considered:
  - ➔ Synchronization of non-ambient parameters and XRD scans
  - ➔ Measurement and control of non-ambient parameters (e.g. temperature)
  - ➔ Thermal expansion of the sample and sample holder could cause misalignment
  - ➔ Possible chemical reactions with the sample holder
  - ➔ Rapid structural changes require fast measurements to observe



BASICS OF NA-XRD



- Non-ambient X-ray (NA-XRD) diffraction has become an indispensable technique to understand the behavior of materials under non-ambient conditions

- Properties of materials may significantly change when exposing them to non-ambient conditions

BASICS OF NA-XRD

- Change of chemical and physical properties may lead to a completely different behaviour of the material
- NA-XRD diffraction allows to study a variety of material changes in-situ:

Processes	Application fields
Material formation and structures	Alloys, building materials, drug APIs, catalysts, minerals,…
Annealing due to heat treatment	Alloys, ceramics, polymers,…
Calcination and sintering	Catalysts, MOFs, zeolites,…
(De)hydration processes	Building materials, pharmaceuticals, food industry,…
Material changes during operation	Catalysts, refractory materials, alloy, batteries,…

INSTRUMENTATION

THE ANTON PAAR PORTFOLIO – SPECIFICATION RANGE

- Temperature (-190 °C to 2300 °C)
- Relative Humidity (5 – 95 % RH up to 60 °C)
- Gas environment (vacuum, air, inert and reactive gases)
- Pressure (<10-4 mbar up to 10 bar)
- Mechanical load (Tensile stress up to 600 N)
- Electrical Load (Imax: 1 A; Vmax: 10 V)

INSTRUMENTATION

THE ANTON PAAR NA-XRD ATTACHMENTS FIT TO

- All commercial diffractometers on the market
  - Lab size diffractometers
  - 2-circle and 4-circle goniometers
  - Benchtop diffractometers

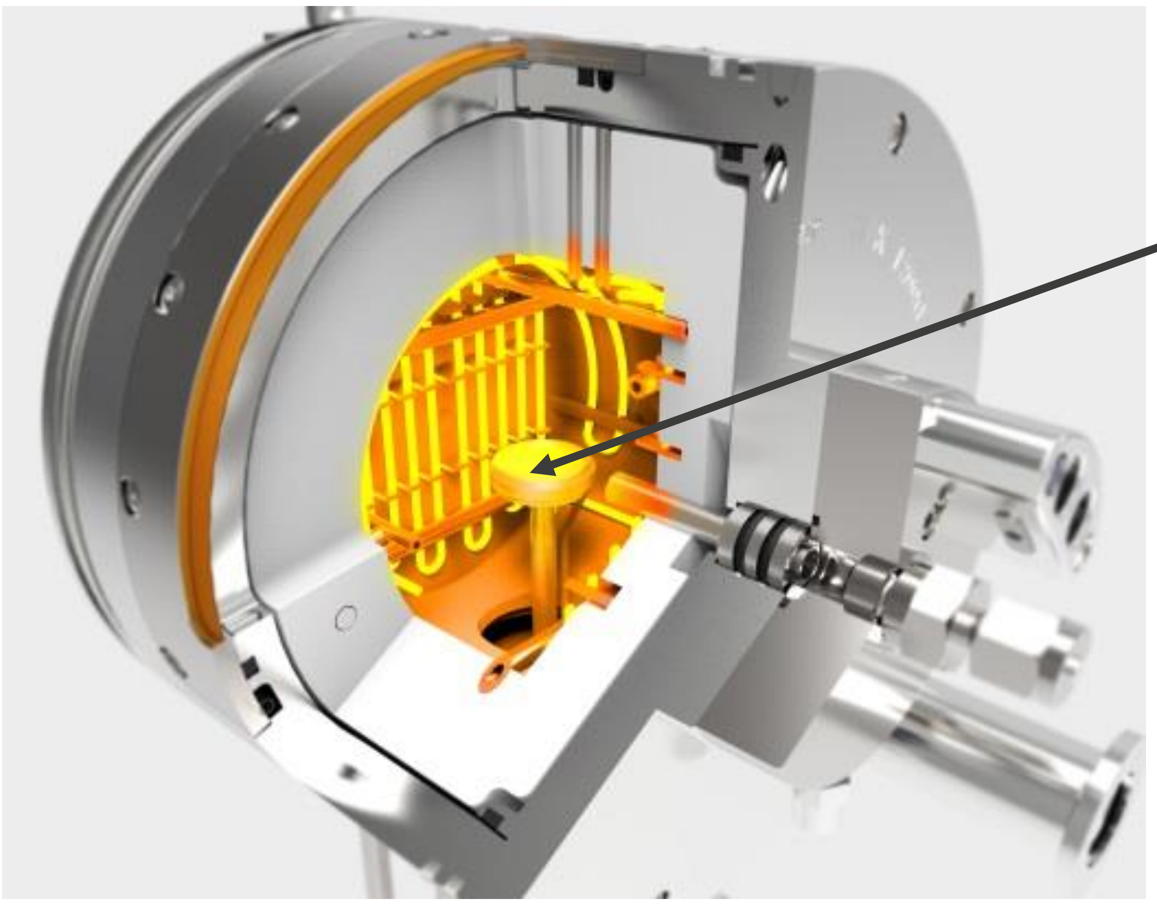
- Also for synchrotron facilities


CONTROL PC
Diffractometer Control
NA-XRD Attachments Control:
– Sending and receiving temperature values
– Heating / cooling power
– Status
CONTROL UNIT
DIFFRACTOMETER
Anton Paar
XRDynamic 500
Z-stage Control:
– Sample Alignment
– Height Alignment
ADAPTER / Z-STAGE
NON-AMBIENT XRD ATTACHMENT
Mounted on
Mounted on

SYSTEM COMPONENTS

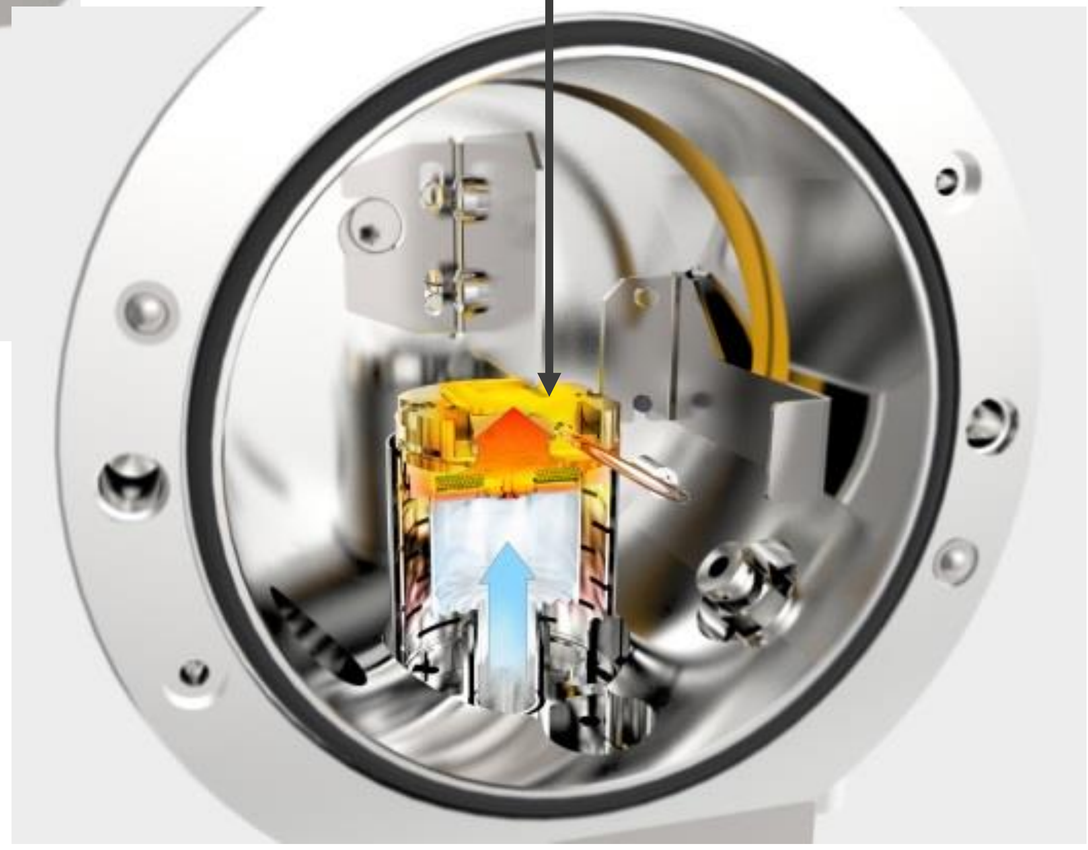
NON-AMBIENT ATTACHMENT – HEATER DESIGNS

ENVIRONMENTAL HEATERS



ALL-SIDE HEAT TRANSFER FROM SURROUNDING HEATER

DIRECT HEATERS

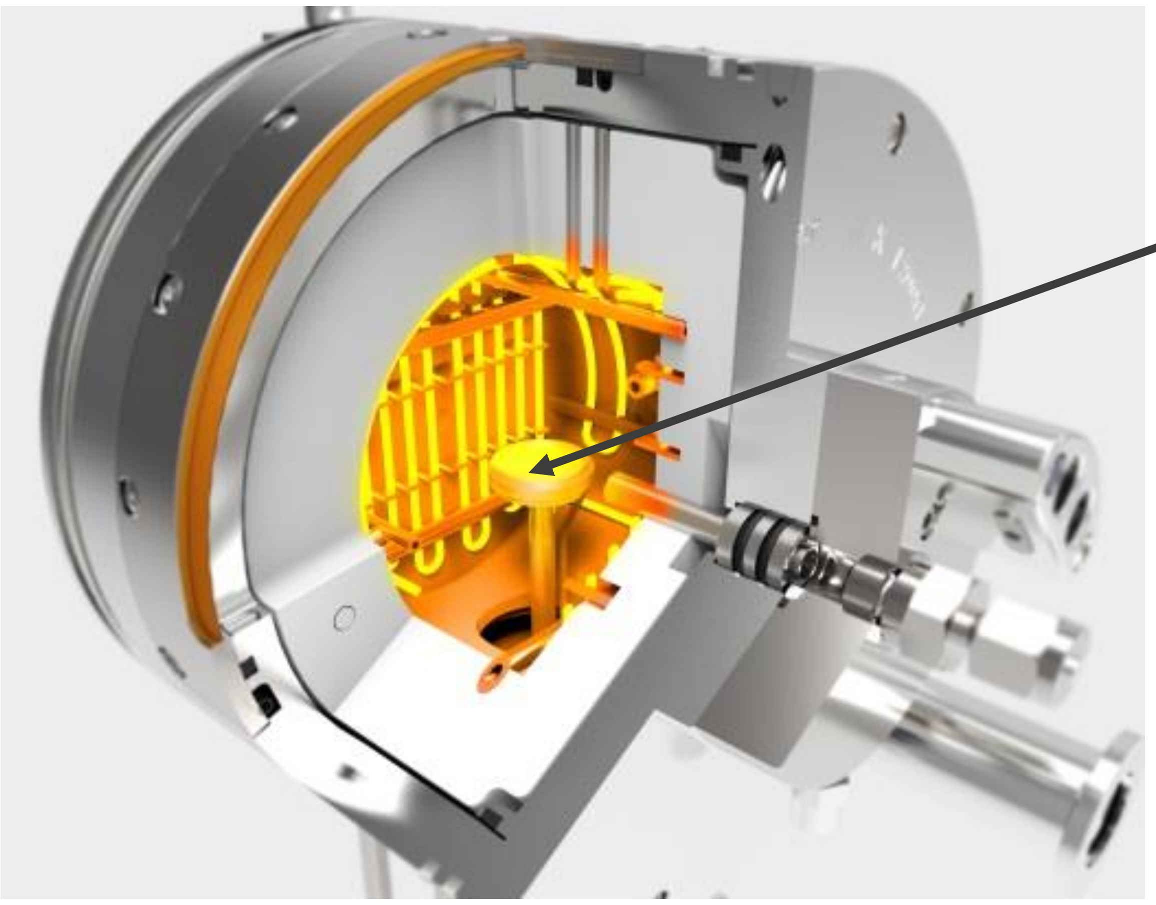


ONE-SIDE HEAT TRANSFERFROM HEATER BELOW THROUGH CONTACT SURFACE

SYSTEM COMPONENTS

NON-AMBIENT ATTACHMENT – HEATER DESIGNS

ENVIRONMENTAL HEATERS



RT TO 1200 °C

DIRECT HEATERS

STRIP HEATERS(1): **RT TO 2300 °C**

HETAING PLATES / HEATER COOLER COMBINATIONS(2): **-190 TO 1100 °C**

SYSTEM COMPONENTS

Environmental Heaters	Strip heaters
Advantages	
✓ Good temperature homogeneity	✓ Very high temperatures possible
✓ More accurate sample temperature measurement	✓ Very fast heating / cooling possible
✓ Easy sample exchange	✓ Simpler design
✓ Reaction of sample holder and specimen can be avoided using inert sample holder materials	✓ Temperature control less dependent on the atmosphere in the chamber
✓ Sample spinning possible	
Disadvantages	
✗ Sample holder expansion	✗ Sample preparation difficult
✗ Slower heating / cooling rates	✗ Less sample temperature unifomity
✗ Decreased upper T-limit	✗ Higher sample temperature deviation
	✗ Reactions between sample and sample holder possible (especially for strip heaters)

SYSTEM COMPONENTS

NON-AMBIENT ATTACHMENT – HEATER DESIGNS

SYSTEM COMPONENTS

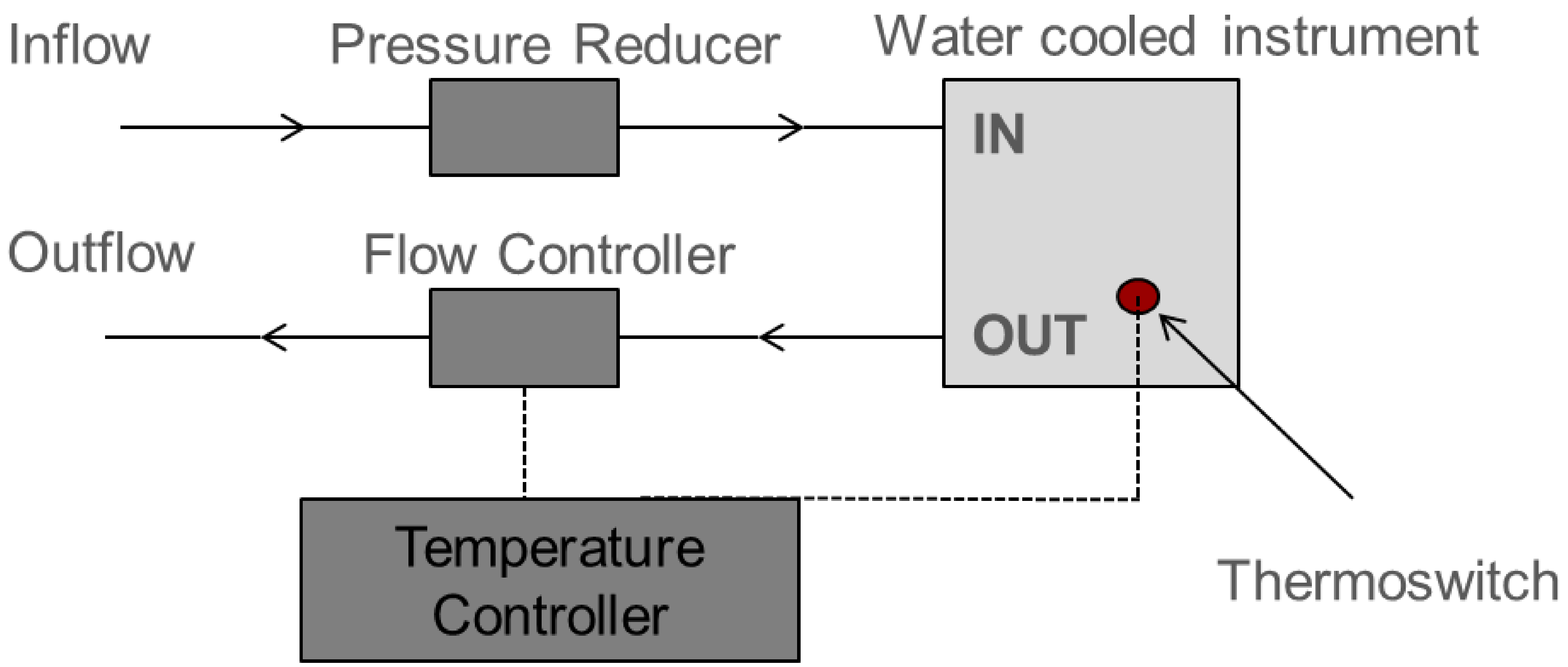
TEMPERATURE CONTROL UNITS

- Converts the signal from temperature sensor into a temperature value, displays the value and transmits it to the control PC
- Provides controlled heating power with
- Power electronics
- Controller firmware
- Controls the safety loops of the instrument
- Cooling water, housing T, sensor function, ...

SYSTEM COMPONENTS

SAFETY PRECAUTIONS

- **Water flow controller:** heating power is switched off in case of insufficient water flow
- **Thermoswitch:** heating power is switched off in case of too high housing temperature
- **Microswitches:** heating power is switched off in case of no detection
  - **HTK 1200N:** detection of sample holder flange
  - **TTK 600:** detection of the heater part
  - **HTK 16N / 2000N:** detection of high-current cable, lid



SYSTEM COMPONENTS

OVERVIEW OF TEMPERATURE CONTROL UNITS

- **Since beginning of 2018 (nearly) all instruments are delivered with CCU-type temperature controllers:**
  - CCU 100: TTK 600, CHCplus, DHS 1100, DCS 500
  - CCU 750: XRK 900
  - CCU 1000: HTK 1200N
  - CCU 2000: HTK16N, HTK 2000N
- **Exceptions (but already discontinued):**
  - TCU 60M: MHC-trans (discontinued)
  - TCU 900: HPC 900

TCU Temperature Control Unit
CCU Combined Control Unit

SYSTEM COMPONENTS

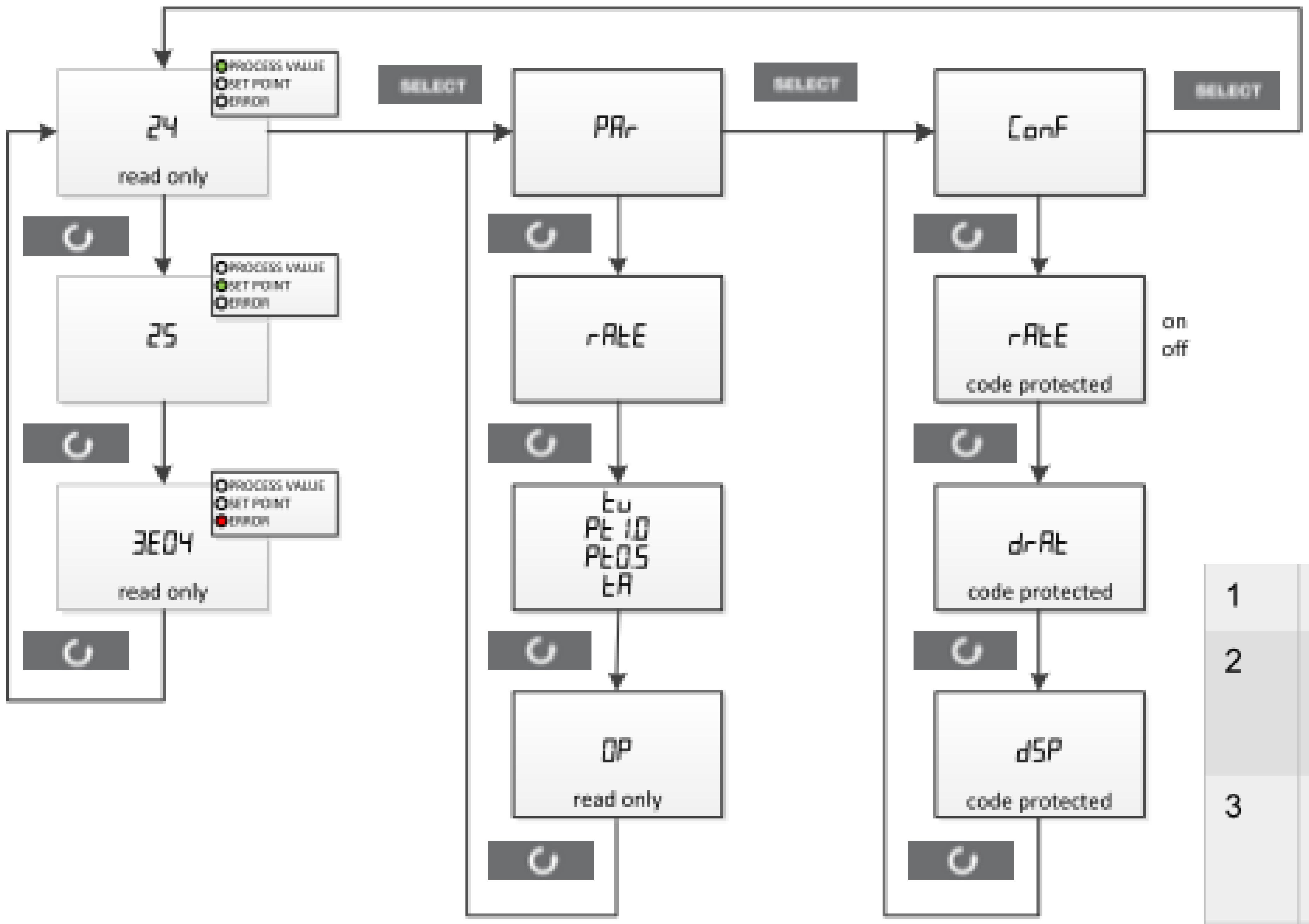
ADVANTAGES OF CCU COMPARED TO TCU

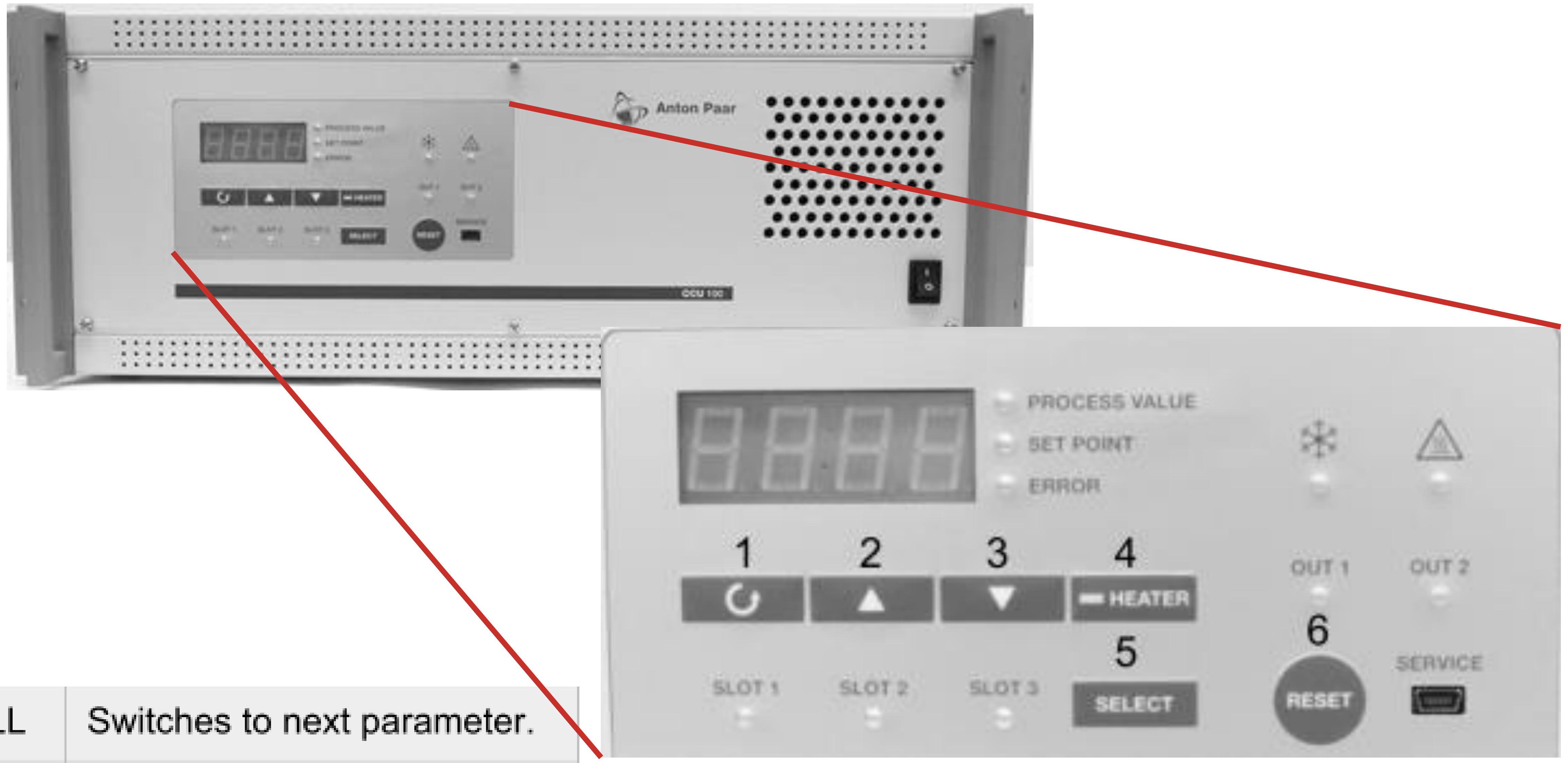
- No Eurotherm controller
- Improved control algorithm
- Easy FW update via USB connector
- Simplified connection
- Multiple instruments with one controller
  - Slot – system: up to three instruments

TCU 60M

CCU 100

SYSTEM COMPONENTS



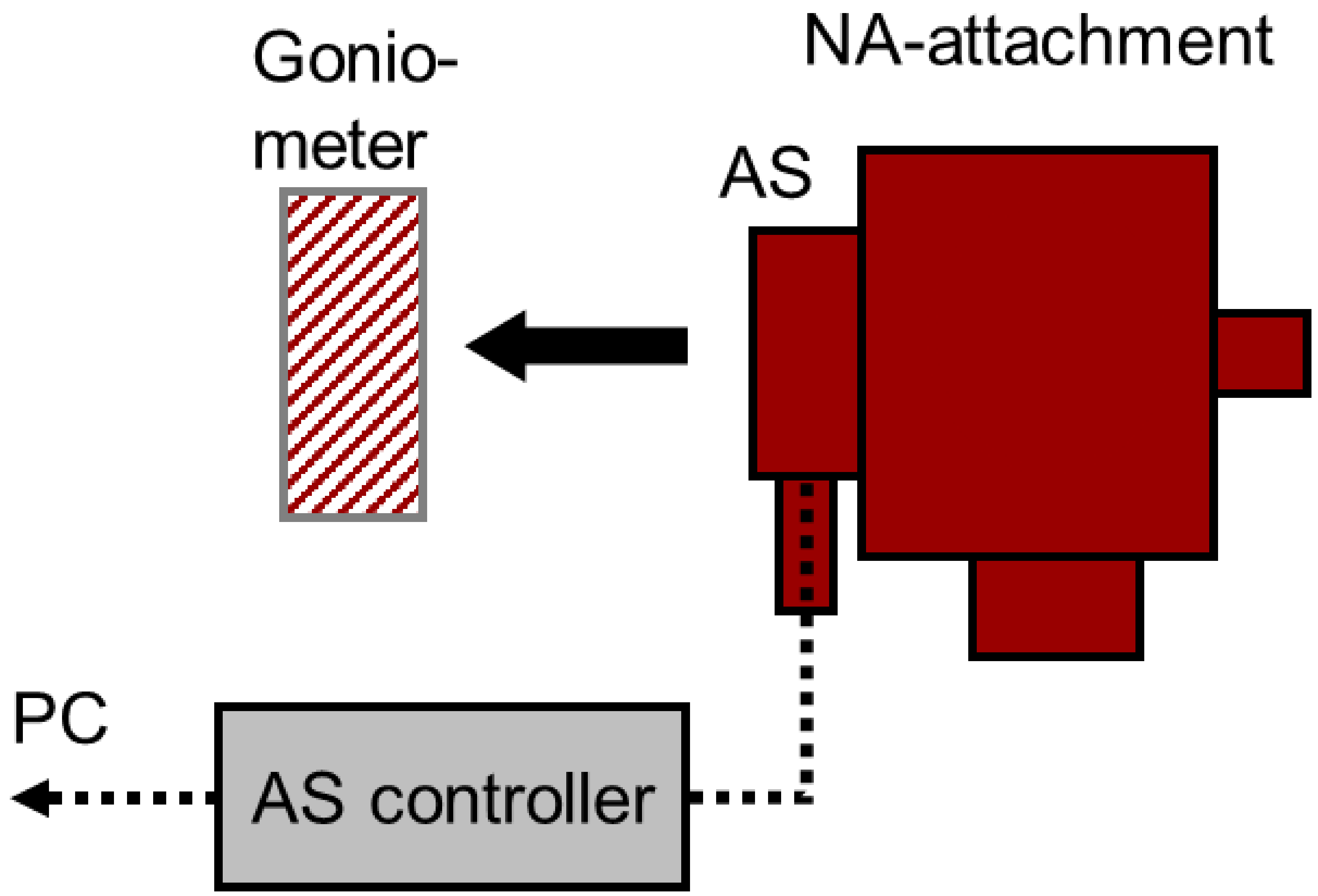


1	SCROLL	Switches to next parameter.
2	UP	Increases the value of the currently displayed parameter.
3	DOWN	Decreases the value of the currently displayed parameter.
4	HEATER	Switches the heater on and off.
5	SELECT	Short: selects a parameter. Long: selects a slot.
6	RESET	Resets an error.

SYSTEM COMPONENTS

ADAPTER AND Z-STAGE

- Adapters for automatic height adjustment
  - Comes from diffractometer manufacturer
    e.g. Empyrean with z-Stage from Malvern Panalytical
  - PC-controllable alignment stage (AS) from Anton Paar
    e.g. X`Pert from Malvern Panalytical



SYSTEM COMPONENTS

SAMPLE HEIGHT ALIGNMENT

- The majority of materials expand during heating.
- This is also true for the sample holders of a non-ambient XRD attachment.
- In combination with the expansion of the sample (minor compared to expansion of the sample holder), the sample surface may move out of the focusing circle of the goniometer (in Bragg-Brentano geometry) during a non-ambient experiment.

This leads to a significant peak shift in the diffractogram.

SYSTEM COMPONENTS

SAMPLE HEIGHT ALIGNMENT

- Ignore sample displacement
  - Problematic for subsequent data analysis
- Correct data directly with diffractometer software
  - For displacements < 0.1 mm
  - Include displacement error in data refinement
- Use parallel beam geometry to avoid peak shift
  - Loss of resolution and loss of measuring speed
- Correct displacement during measurement
  - Manual re-alignment or automated compensation

SYSTEM COMPONENTS

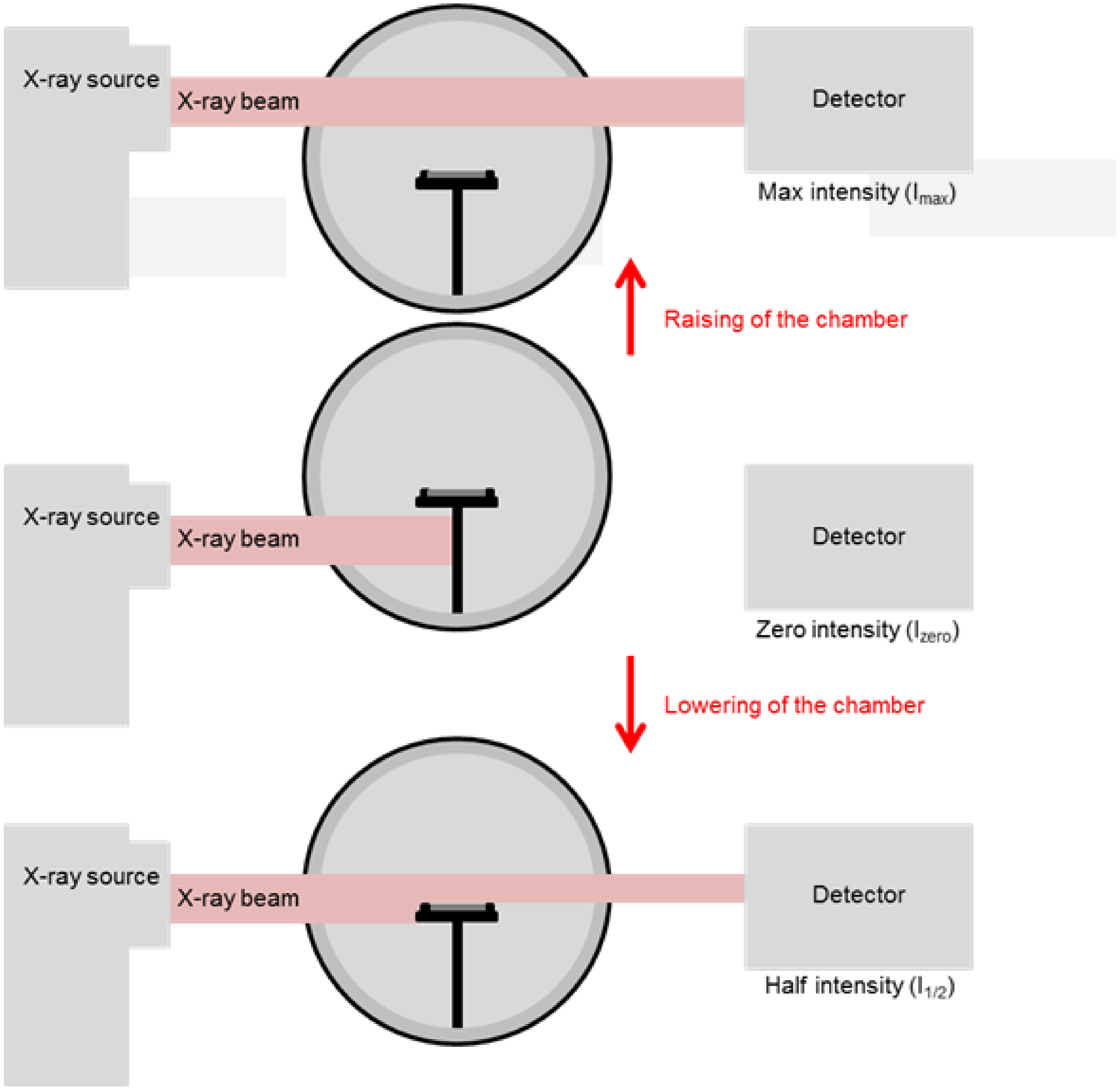
ADAPTER AND Z-STAGE

- TCU/CCU sends T- value to diffractometer software
- Software writes a T file
- APSM reads the sample holder temperature from the file
- APSM corrects the height of the sample stage acc. to pre-selected compensation table

SYSTEM COMPONENTS

HEIGHT OR Z-CALIBRATION

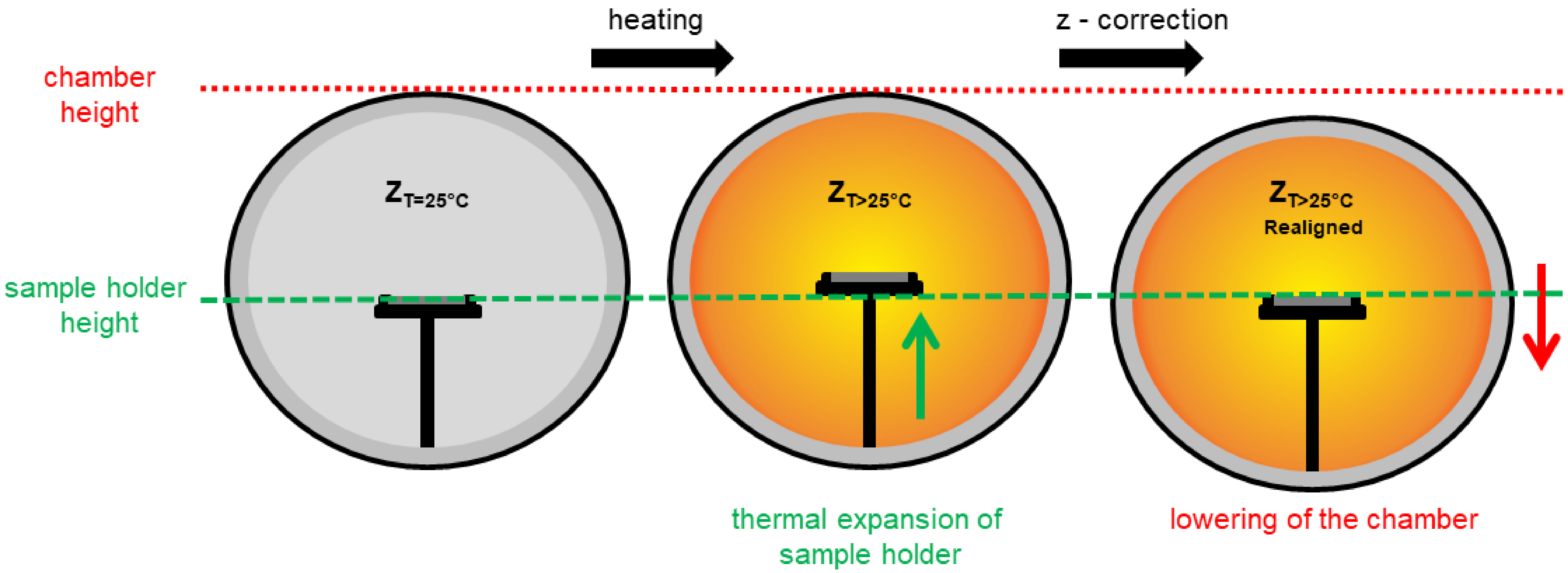
- Find I_{max}
- Find I_{zero}
- Find $I_{1/2}$



SYSTEM COMPONENTS

HEIGHT OR Z-CALIBRATION

- Approximate correction with the factory correlation tables or accurate correlation with your own values (determined as described)
- Manual or automated (Z-stage) correction of Z-position possible



SYSTEM COMPONENTS

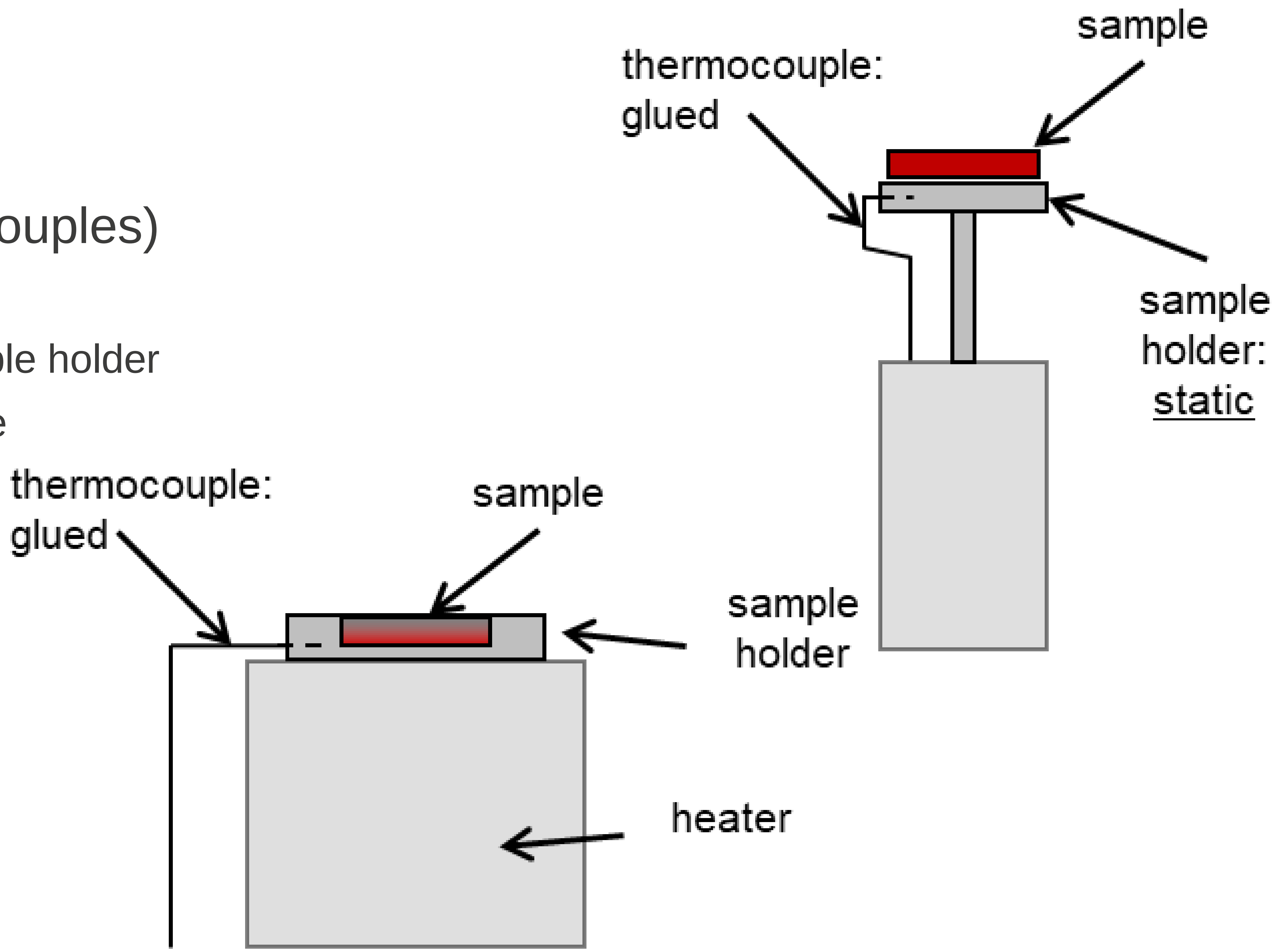
TEMPERATURE MEASUREMENT

- Temperature sensors (RTDs or thermocouples)
  - Temperature measurement of the sample holder and not the sample
  - Highest reproducibility
  - Independent from conditions inside the sample chamber (atmosphere type, pressure, humidity,...)
- Optical methods
  - IR camera or pyrometer
    - Emission coefficient (changing with temperature and surface properties)
    - Influence of window of stage housing

SYSTEM COMPONENTS

TEMPERATURE MEASUREMENT

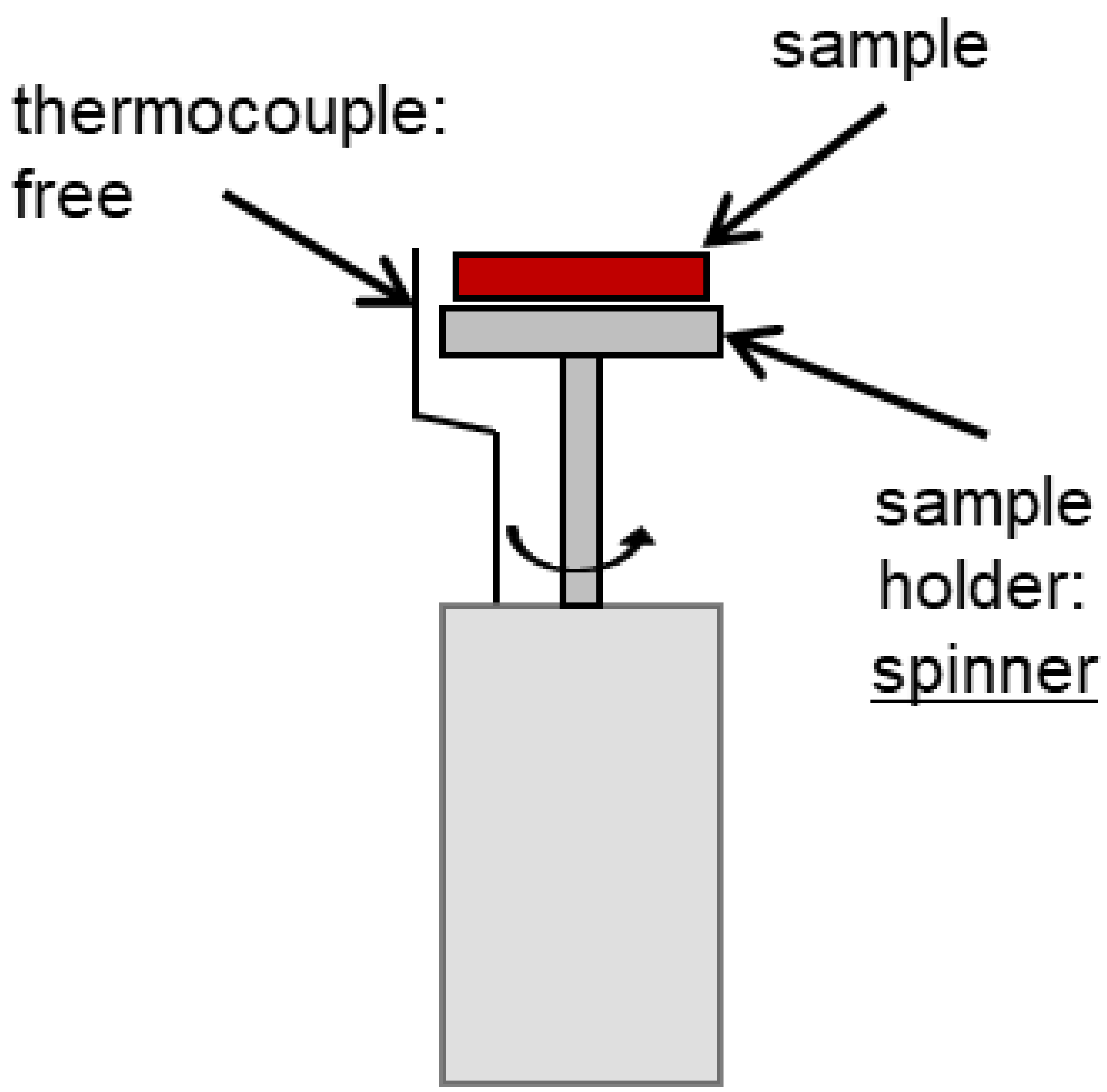
- Temperature sensors (RTDs or thermocouples)
  - Inside / on the sample holder
    - Thermal contact between sensor and sample holder
    - Heat transfer from sample holder to sample



SYSTEM COMPONENTS

TEMPERATURE MEASUREMENT

- Temperature sensors (RTDs or thermocouples)
  - Close to the sample but without contact
    - Pollution of the sensor
    - Sample holder rotation possible

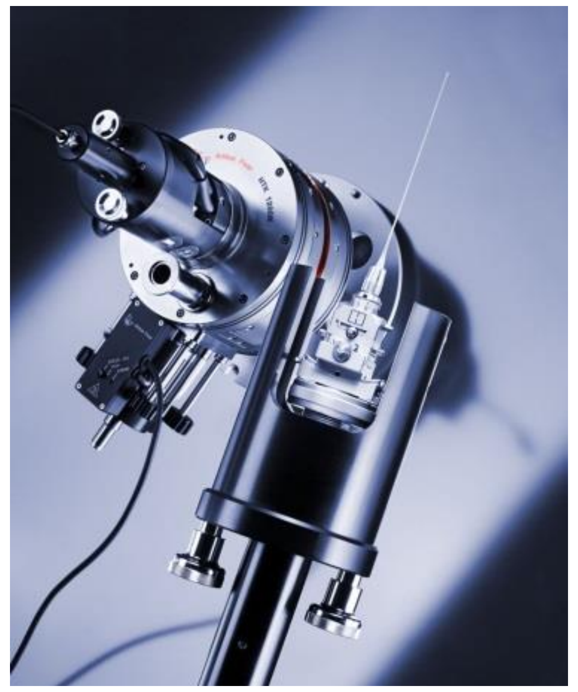


ANTON PAAR PORTFOLIO

Environmental Heaters

XRK 900

HTK 1200N



Direct Heaters

Direct Heaters / Coolers

TTK 600

CHC PLUS+

BTS 150 / 500

Strip Heaters

HTK 16N / HTK 2000N

Heating / Cooling Plates

DCS 500

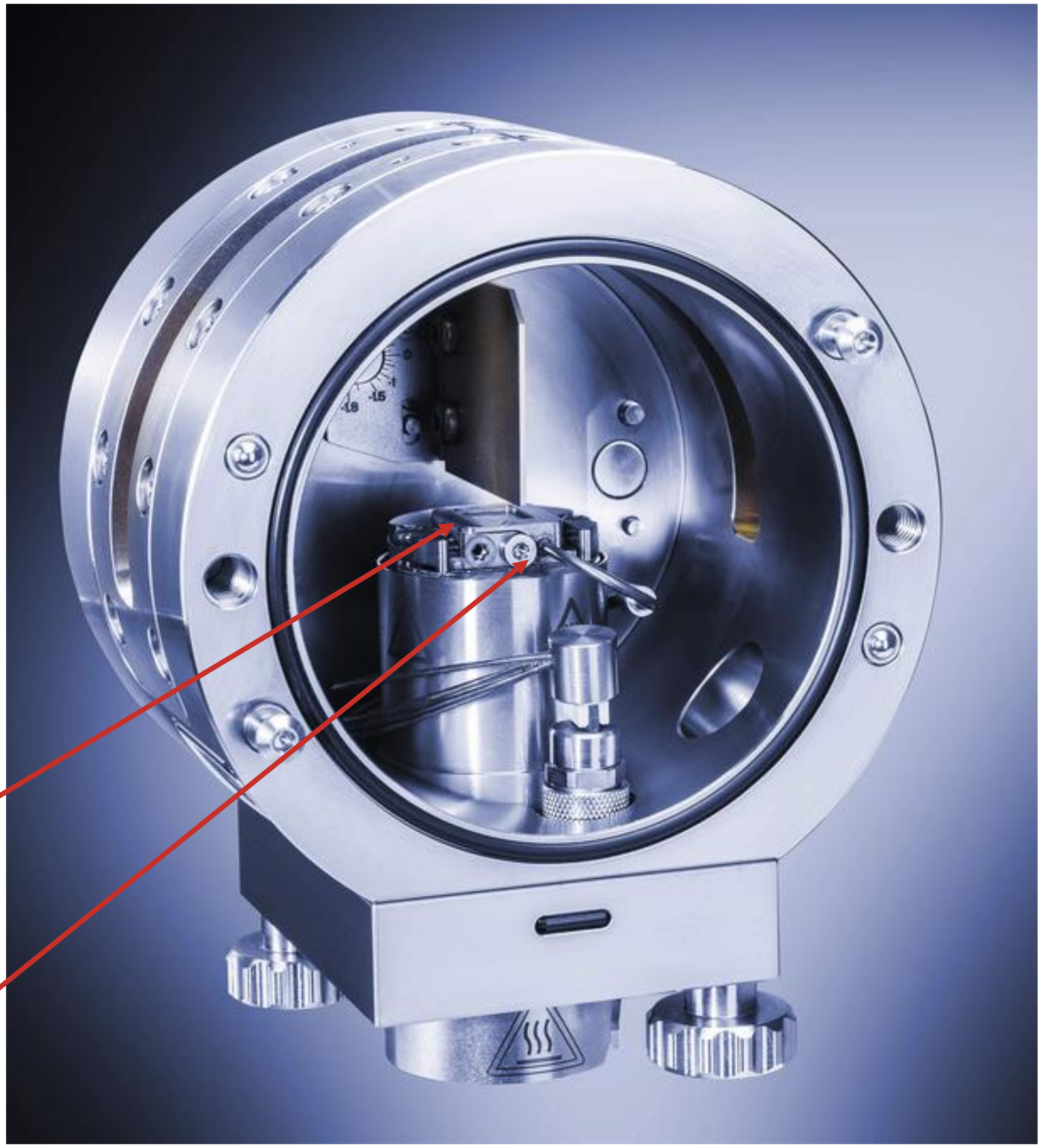
DHS 1100

TEMPERATURE ACCURACY AND VALIDATION

TEMPERATURE ACCURACY

TEMPERATURE ACCURACY

- Specified temperatures always refer to the temperature of the sample holder and not the sample.
- Temperature accuracy is a major concern NA-XRD!
- The location of the measurement and the area under investigation are different!
- Deviation between the measured temperature and the sample surface temperature has to be expected.



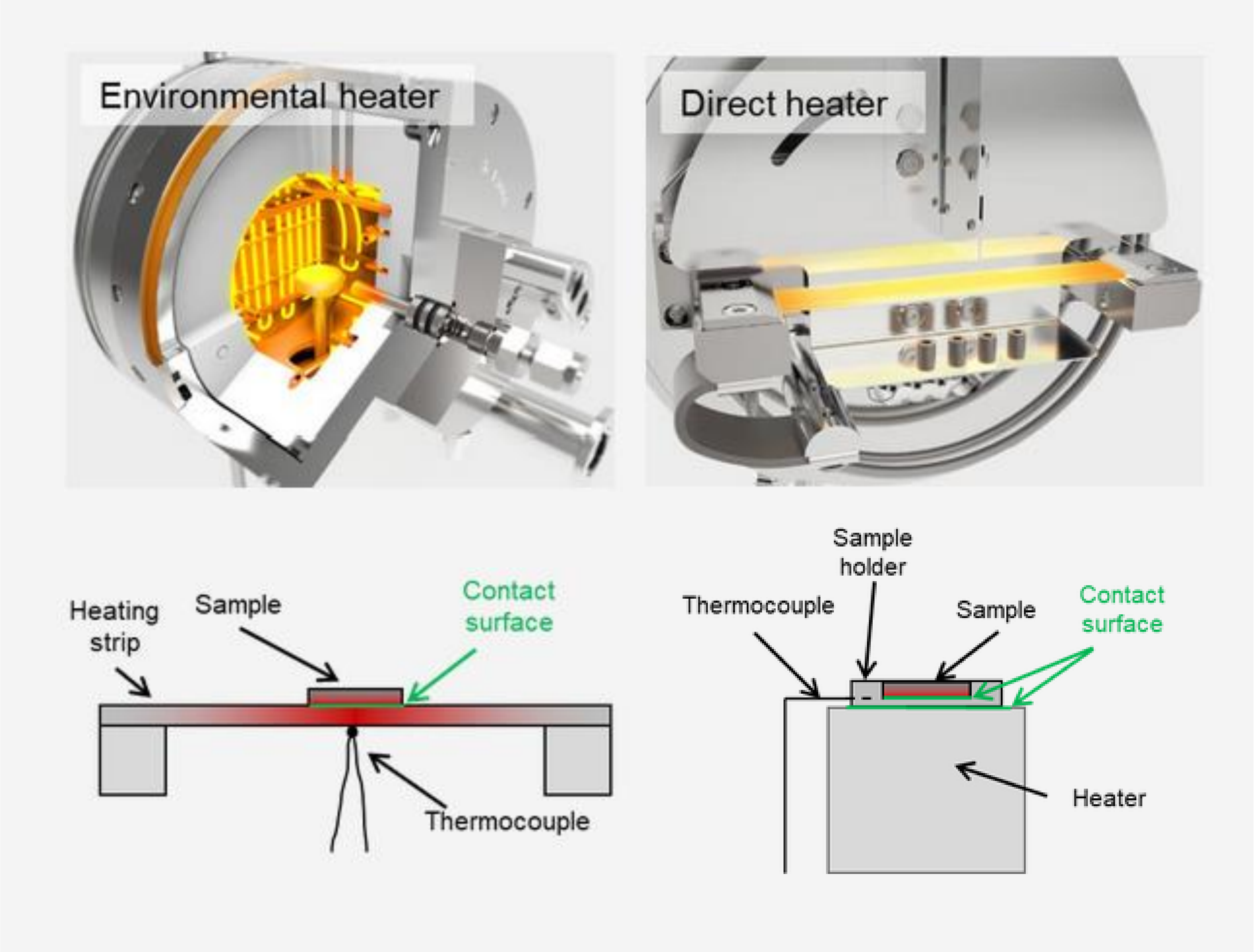
AREA UNDER INVESTIGATION

TEMPERATURE MEASUREMENT

TEMPERATURE ACCURACY

TEMPERATURE ACCURACY

- Design of non-ambient XRD attachment
  - Direct or environmental heater
- Applied atmosphere
  - Vacuum or gas atmosphere
- Thermal properties of the sample
  - Heat conductivity, emissivity, sample thickness
- Contact surface
  - Surface between heater and sample is crucial



TEMPERATURE VALIDATION

TEMPERATURE VALIDATION

› Determine the relation between temperature output of the stage control unit and true temperature of the sample surface.

› Reference materials are required.

› Validation methods:

  › Phase transition: Monitor a crystallographic transformation or sample melting and compare the measured transition with tabulated values

  › Thermal expansion: Measure the change of the lattice parameter(s) during heating / cooling and compare it with thermal expansion curves from the literature.

Temperature validation is strongly recommended for the particular experimental conditions!

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – PHASE TRANSITION

- Requirements for reference materials
  - Well known transformation temperature
  - Fast phase transformation
  - Reversible transformation
  - No reaction with sample holder (melting)
- Procedure
  - Find best region (ROI) of peak pattern to monitor the transformation
  - Define a short 2θ-scan over the ROI
  - Heat the sample in steps and run a scan at each temperature
  - Plot peak intensity vs. displayed temperature and determine the transformation temperature and compare it to the value from the literature

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – PHASE TRANSITION

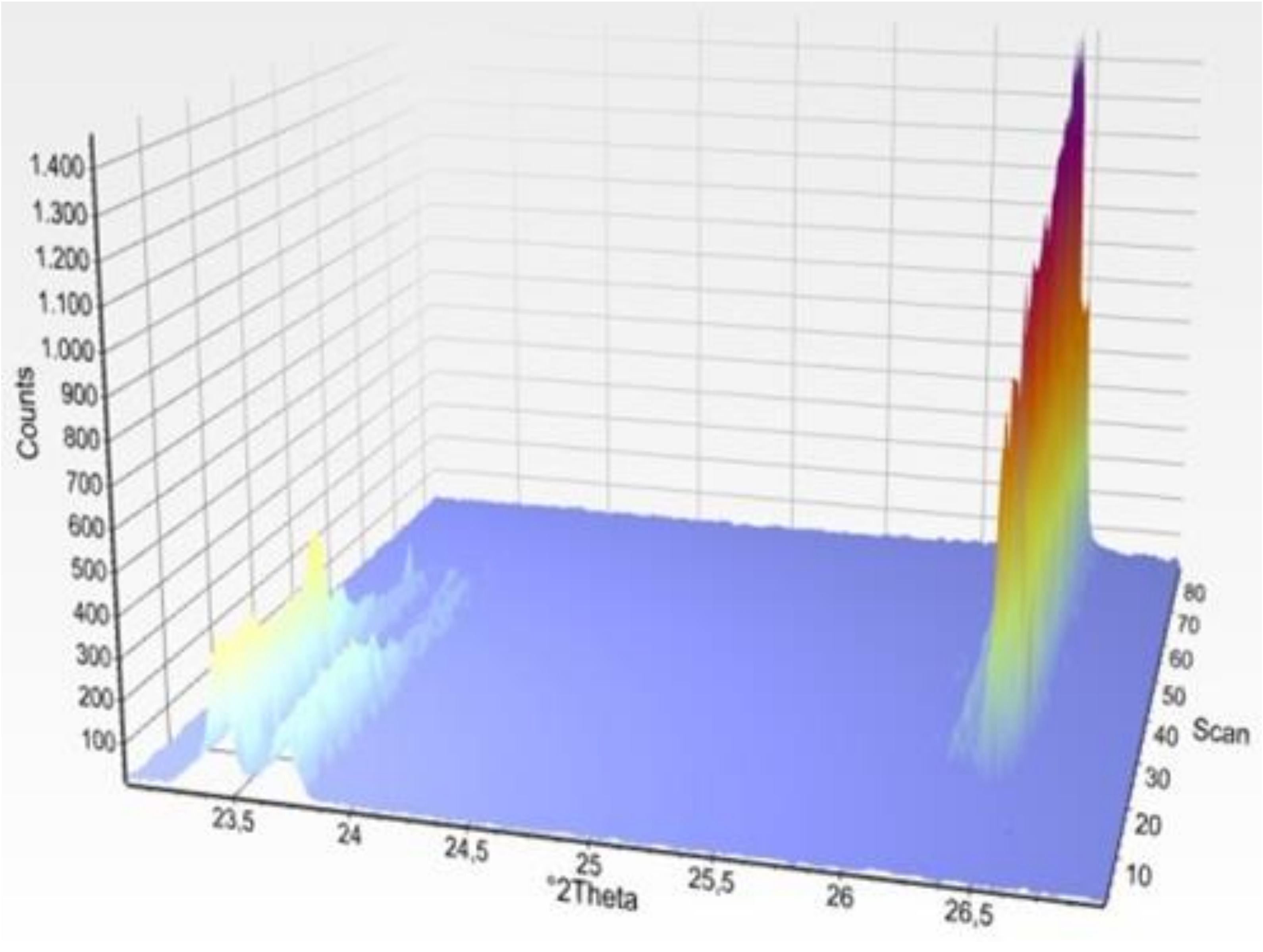
- Advantages and Disadvantages
  - ✓ No special requirements on data quality
  - ✓ Simple data evaluation

  - × Only one (max. a few) temperature values per reference material
  - × Limited availability of feasible phase transformation

TEMPERATURE VALIDATION

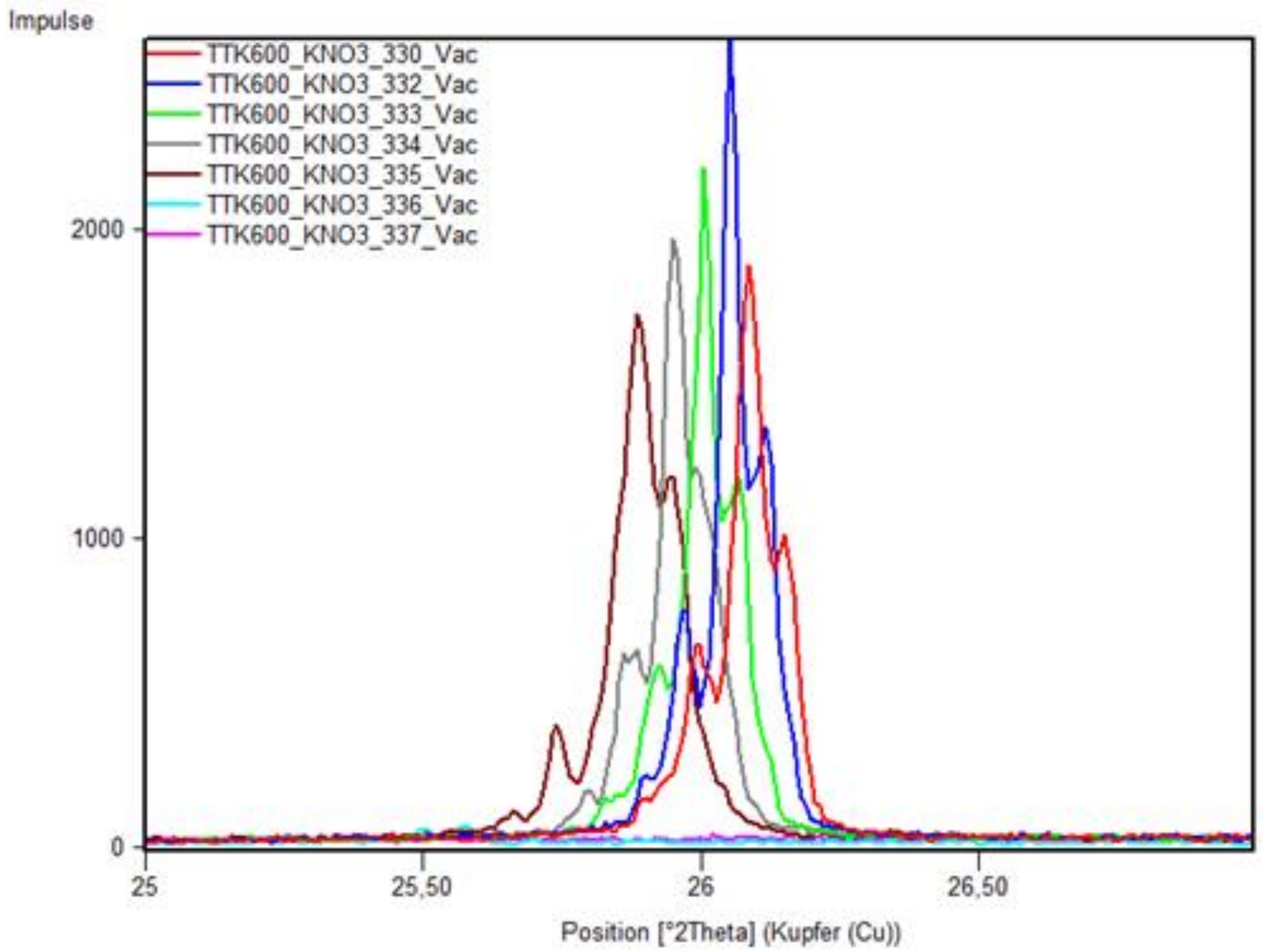
TEMPERATURE VALIDATION – PHASE TRANSITION EXAMPLE KNO_3
USE OF STANDARD SAMPLE HOLDER ONLY

Orthorhombic to trigonal: ~129 °C



Result: 134 °C (deviation of 5 °C)

Melting point: ~334 °C

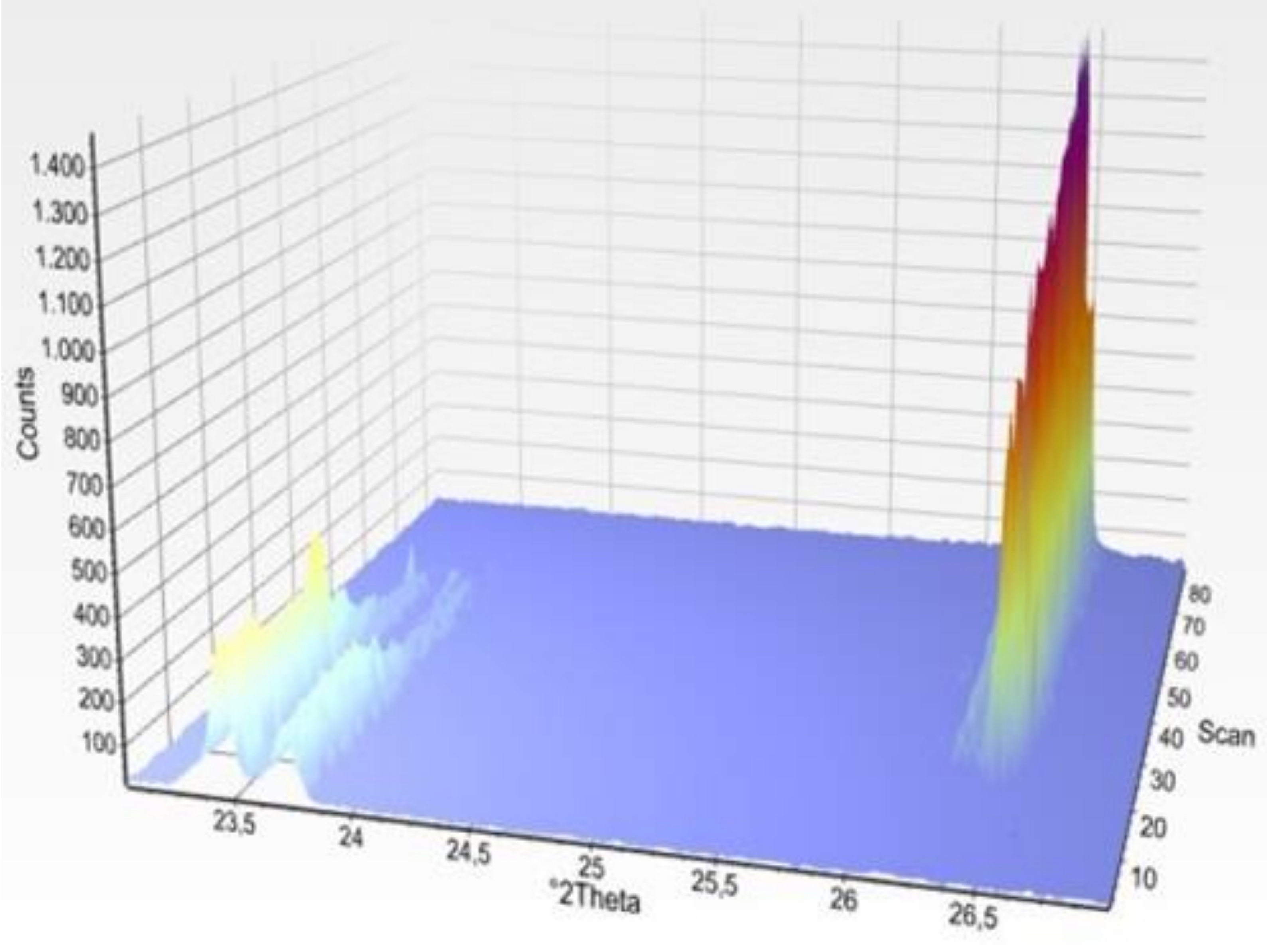


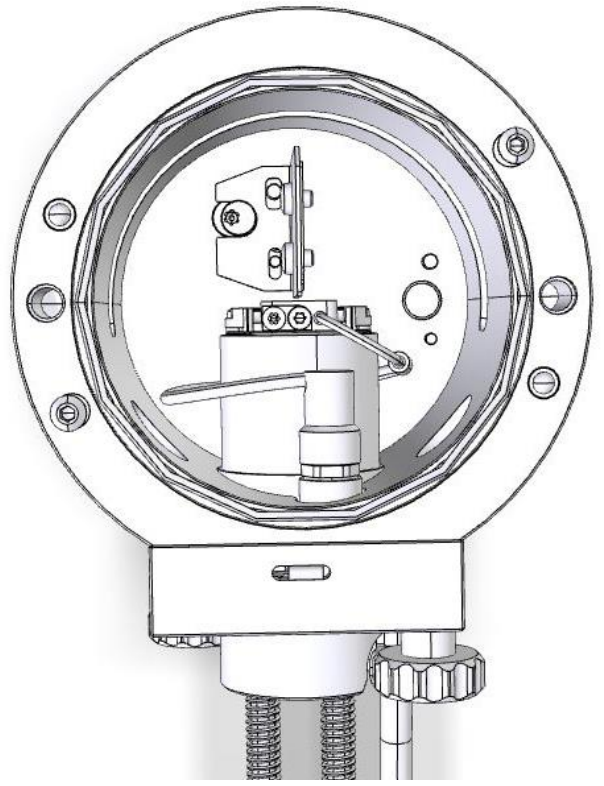
Result: 336 °C (deviation of 2 °C)

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – PHASE TRANSITION EXAMPLE KNO_3
USE OF STANDARD SAMPLE HOLDER WITH HEATING ENVIRONMENT

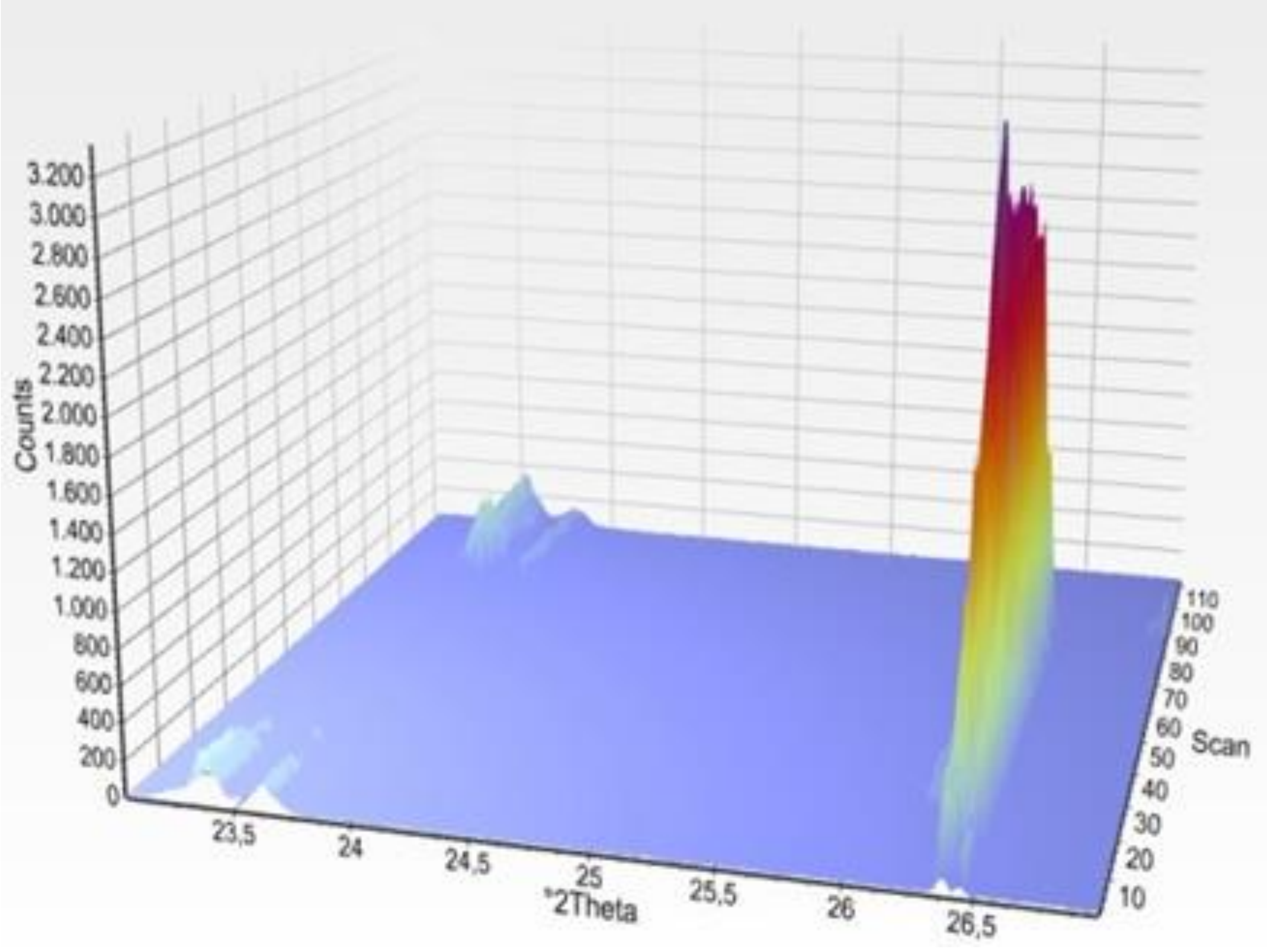
Orthorhombic to trigonal: ~129 °C

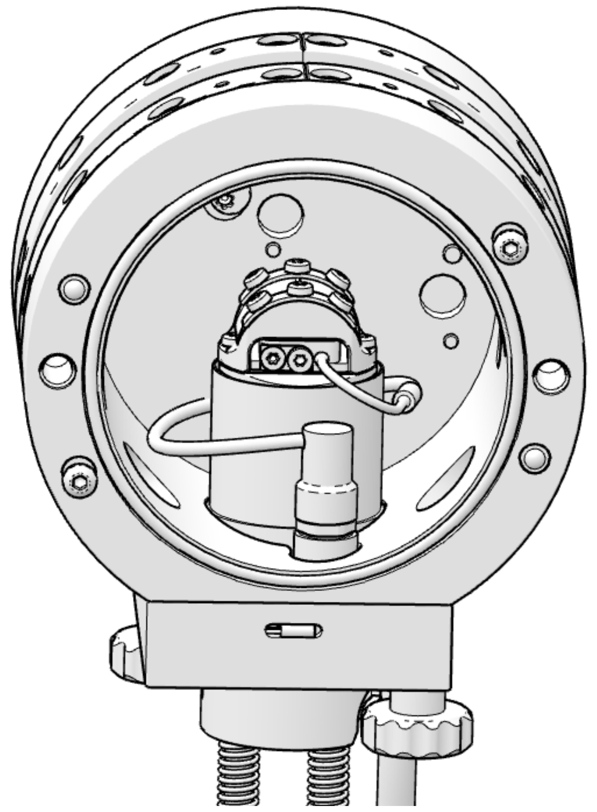




Result: 134 °C (deviation of 5 °C)

with heating environment



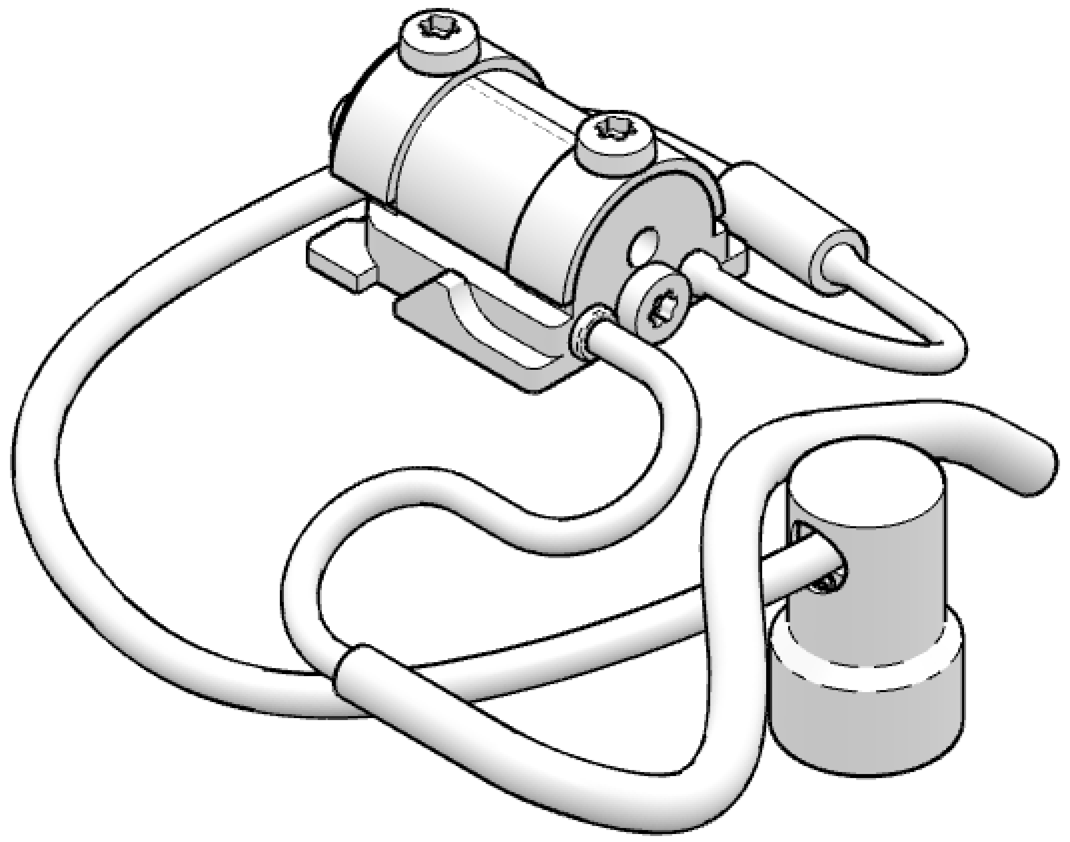


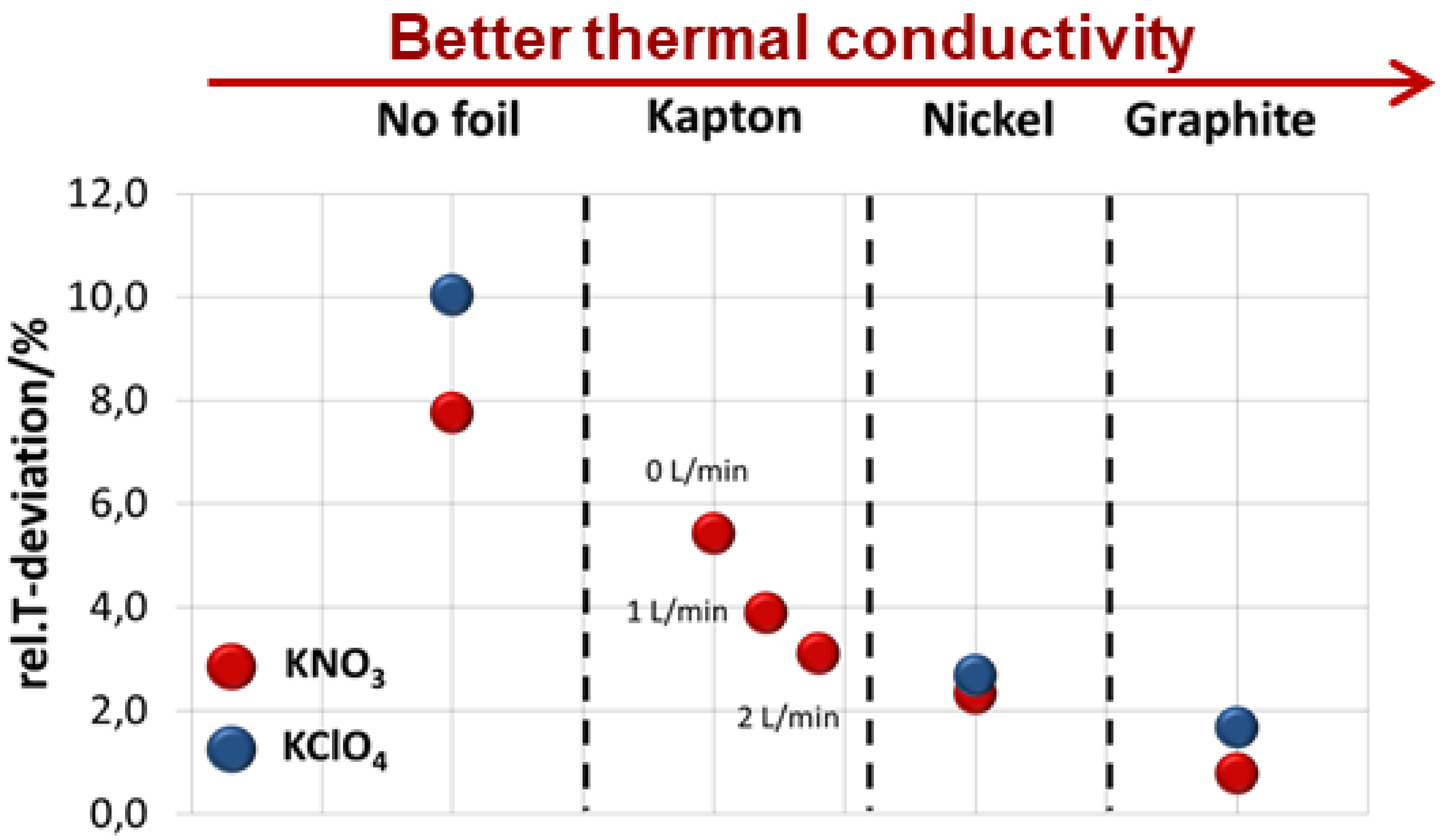
Result: 129 °C (deviation of 0 °C)

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – PHASE TRANSITION EXAMPLE KNO_3 AND $KClO_4$ WITH CAPILLARY SAMPLE HOLDER

- Foil covered sample and convection heater
- Phase transition of KNO3 (129 °C) and KClO4 (299 °C)
- Deviation depends on thermal conductivity of foil material
- Further improvement by using the convection heater (opt. 2L/min)



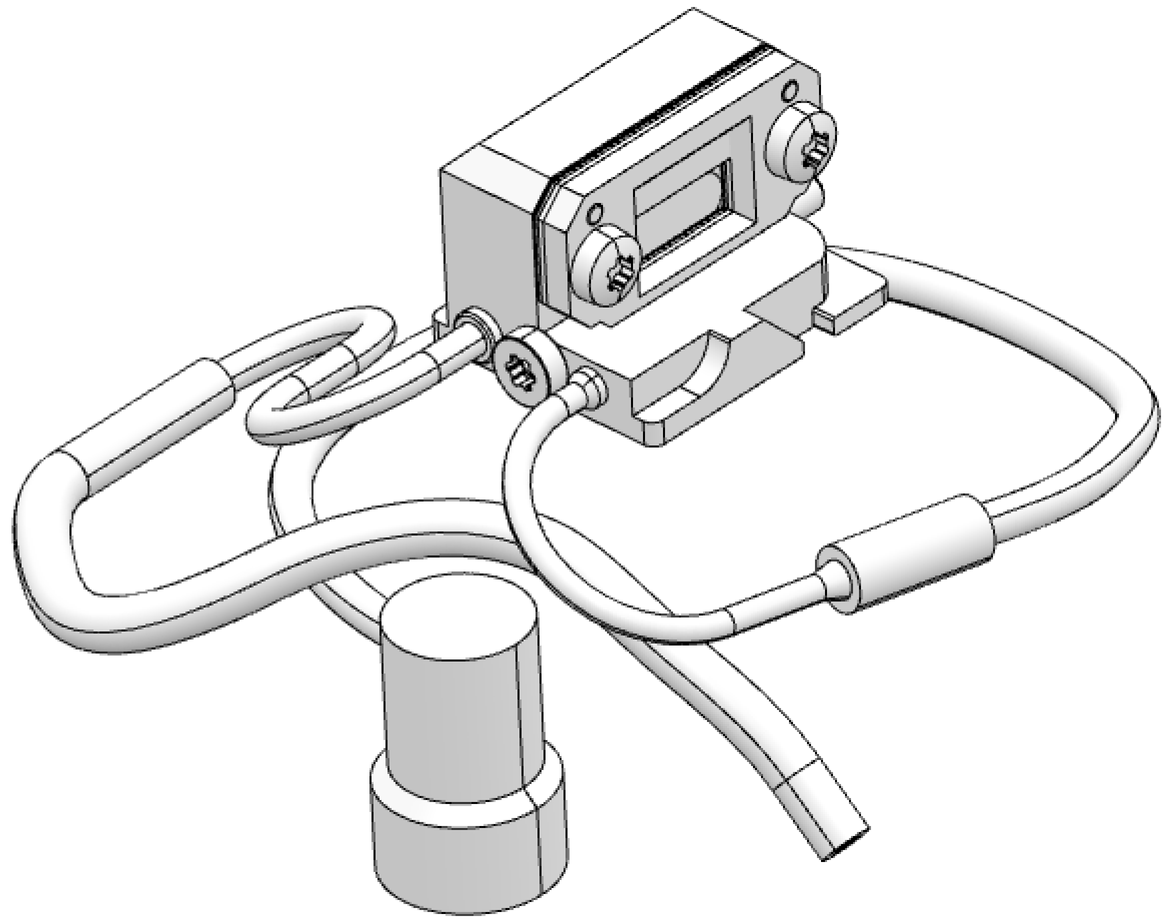


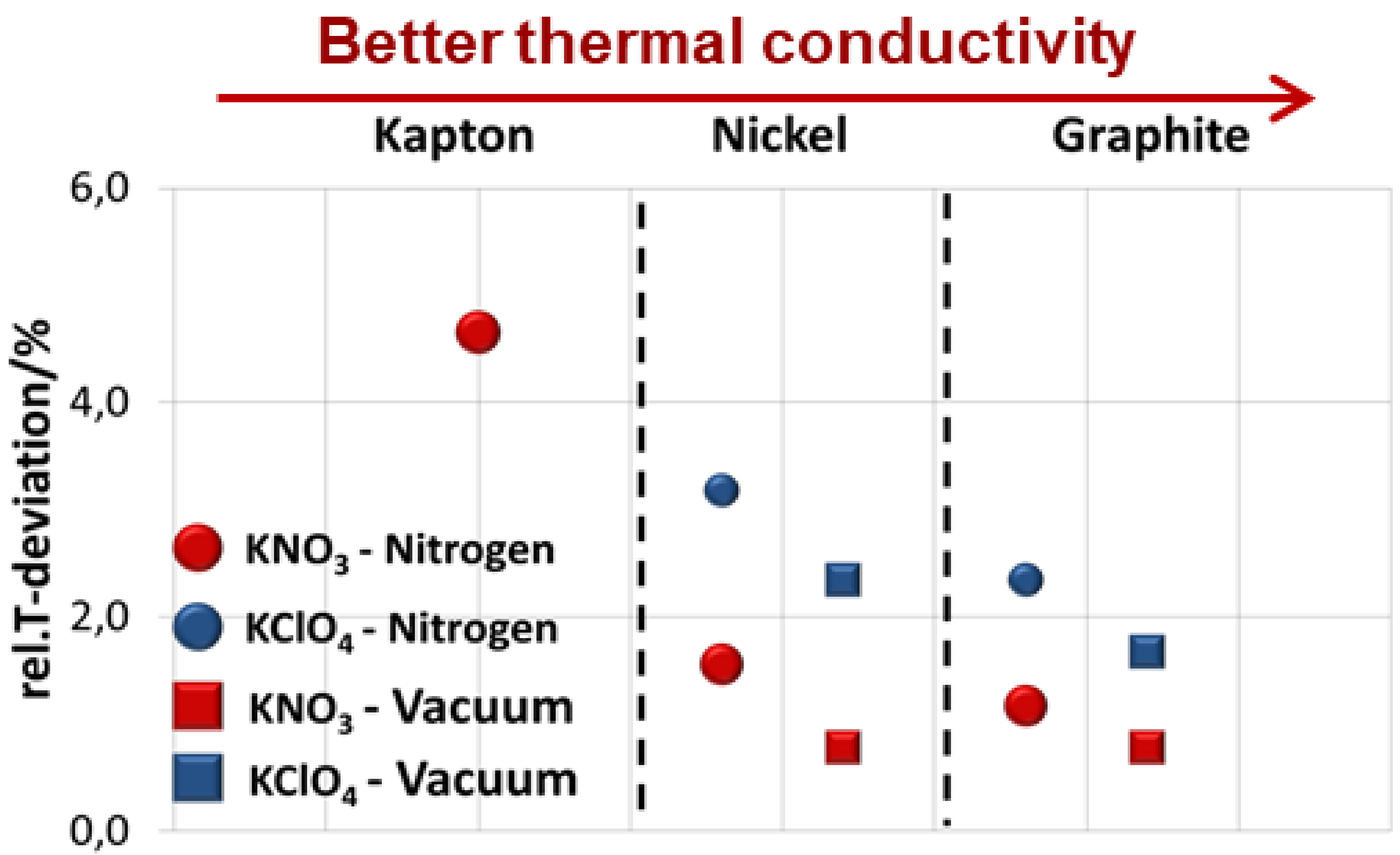
- Thermal conductivity:
  - Kapton: ~ 0.2 W/mK
  - Nickel: ~ 80 W/mK
  - Graphite: ~ 140 W/mK

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – PHASE TRANSITION EXAMPLE KNO_3 AND $KClO_4$ WITH TRANSMISSION SAMPLE HOLDER

- Foil covered sample and convection heater
- Phase transition of KNO3 (129 °C) and KClO4 (299 °C)
- Deviation depends on thermal conductivity of foil material and atmosphere
- Use of convection heating beneficial for Kapton foil





TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – PHASE TRANSITION REFERENCE MATERIALS

Substance	Transition Temp [°C]:	Type [1]	Lit. [2]	Substance	Transition Temp [°C]:	Type [1]	Lit. [2]
NH_4NO_3	54	p.t.	1	SiO_2	573	p.t.	1
NH_4NO_3	127	p.t.	1	Li_2SO_4	577,85	p.t.	3
KNO_3	128,7	p.t.	2	K_2SO_4	584	p.t.	1
In	156,5985	m.p.	3	Sb	630,5	m.p.	4
$RbNO_3$	166	p.t.	2	Rb_2SO_4	653	p.t.	5
$RbNO_3$	222,7	p.t.	2	Al	660,323	m.p.	3
Sn	231,928	m.p.	3	KCl	776	m.p.	4
Bi	271,4	m.p.	2	NaCl	804	m.p.	4
$RbNO_3$	285	p.t.	1	Bi_2O_3	820	m.p.	4
$KClO_4$	299,4	p.t.	2	Ag	961,78	m.p.	3
Cd	321	m.p.	2	NaF	988	m.p.	4
Pb	327,46	m.p.	3	Au	1064,18	m.p.	3
KNO_3	334	m.p.	2	K_2SO_4	1069	m.p.	4
Zn	419,527	m.p.	3	Cu	1083	m.p.	4
$AgSO_4$	426,4	p.t.	2	CaF_2	1360	m.p.	4
CuCl	430	m.p.	4	Ca_2SiO_4	1425	p.t.	4
CsCl	476	p.t.	1	Fe	1535	m.p.	4

1. Rodriguez, M.: High-temperature and non-ambient X-ray diffraction. In: Industrial Applications of X-ray diffraction. Eds.: Chung, F.H., Smith, D.K.; 2000.
2. Levin, E.M., Robbins, C.r., McMurdie, H.F.: Phase diagrams for ceramists. American Ceramic Society, Columbus, OH; 1964.
3. Dinnebier, R.E., Billinge, S.J.L.: Powder diffraction: Theory and practice. The Royal Society of Chemistry; 2008.
4. http://catalog.conveyorspneumatic.com/
5. Nau, M.: Elektrische Temperaturemessung mit Thermoelementen und Widerstandsthermometern. Jumo GmbH&Co.KG, Fulda, 2004

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – THERMAL EXPANSION

- Requirements for reference materials
  - Accurately known thermal expansion curves
  - Large thermal expansion coefficients
  - Stable lattice parameters
  - No oxidation
- Procedure
  - Run large range 2θ-scans at 25 °C (reference) and at the desired temperatures
  - Determine the lattice parameters with Rietveld refinement
  - Calculate the relative lattice expansion a(T)/a(25 °C)
  - Use the inverted expansion curve to calculate the true sample temperature and compare it to the displayed scan temperature

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – THERMAL EXPANSION

› Advantages and Disadvantages

- ✓ The complete temperature range can be calibrated with one standard sample
- ✓ Method applicable to very high temperatures

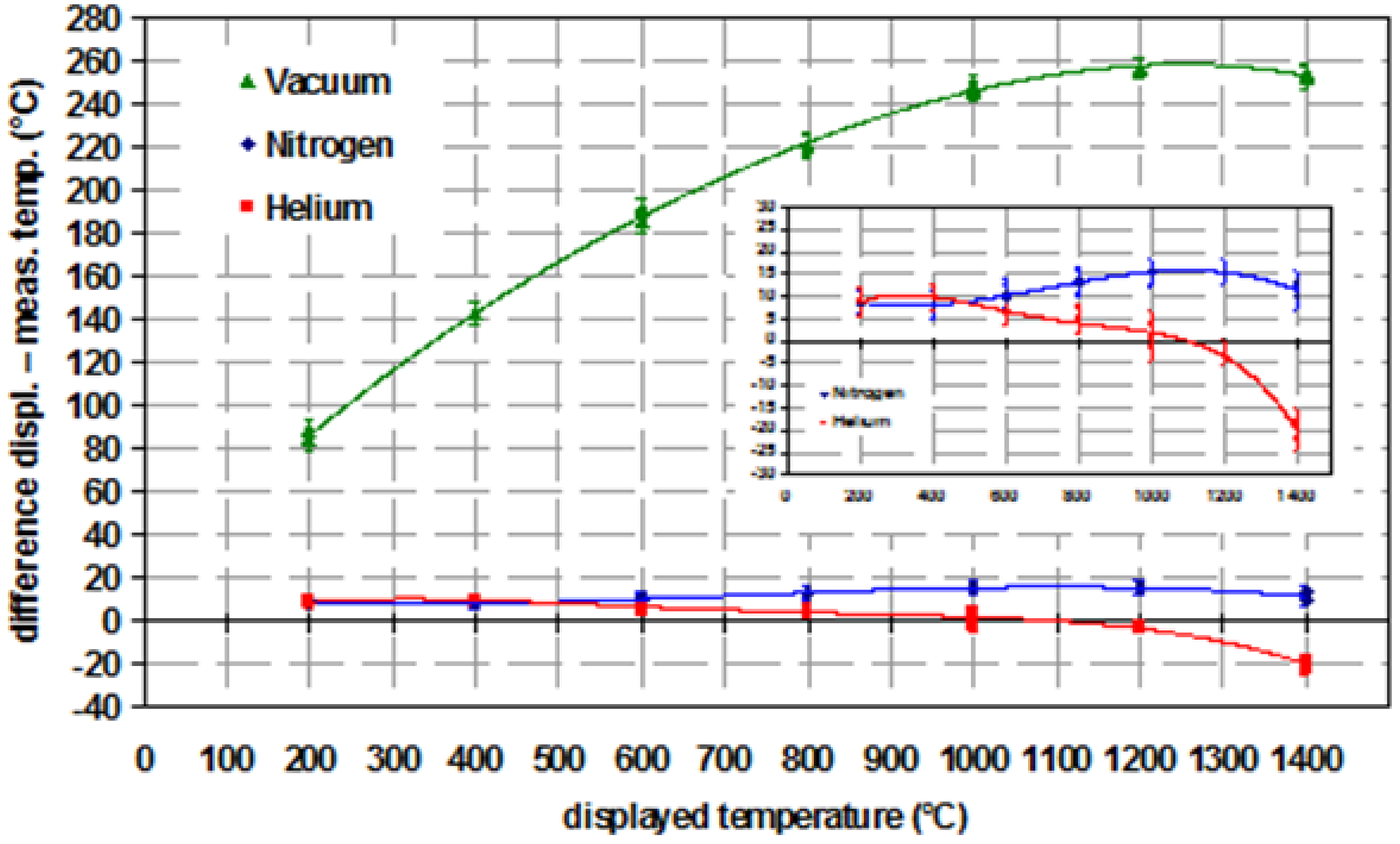
- ○ Good data quality required (refinement)

- ✗ Considerable data evaluation required
- ✗ Inaccurate at low temperatures (< 400 °C) due to small lattice expansion

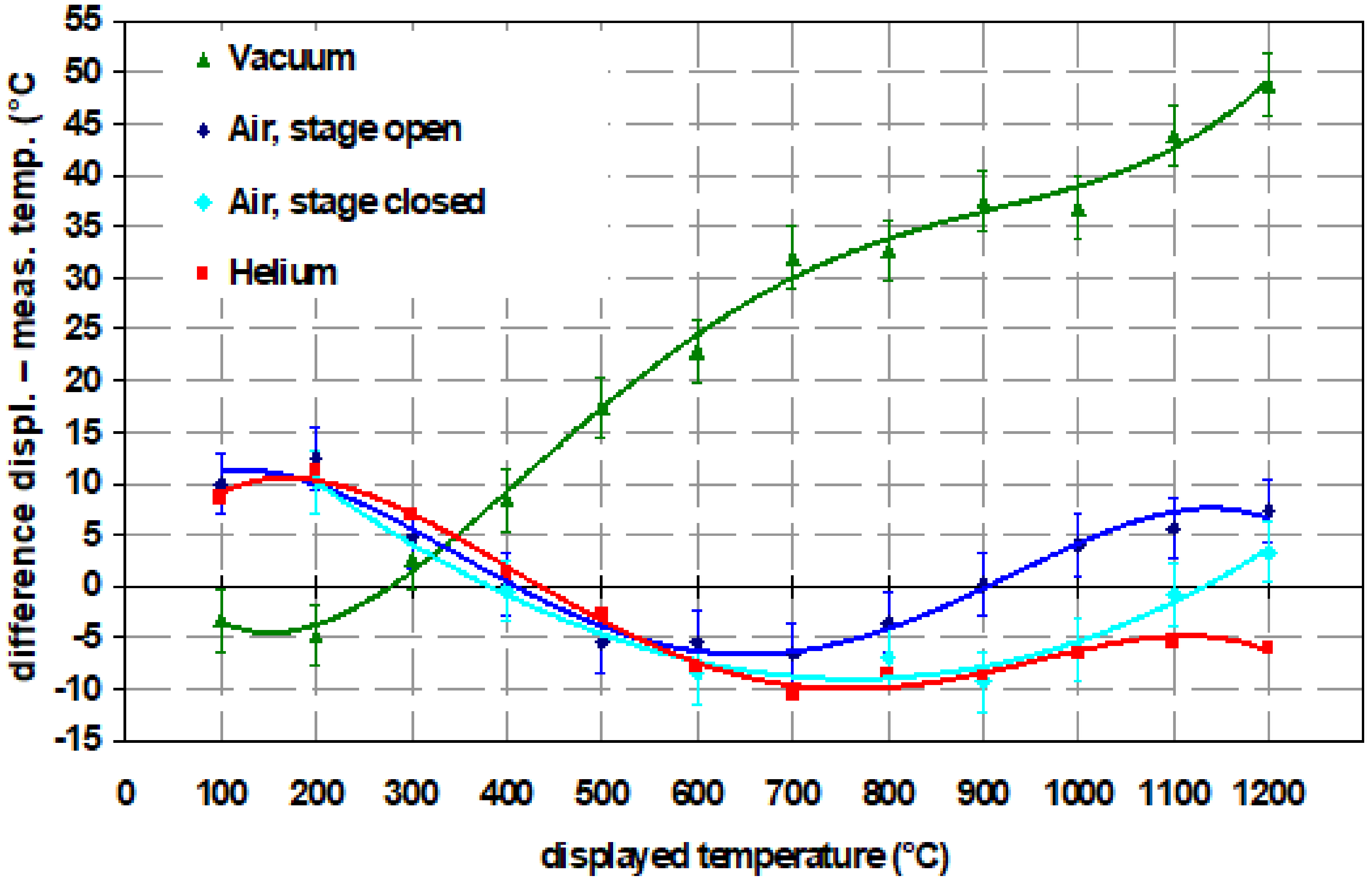
TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – THERMAL EXPANSION (Al_2O_3 c-AXIS) INFLUENCE OF HEATER TYPE

Strip Heater (HTK 16N)



Furnace Heater (HTK 1200N)



stage open: pressure inside chamber remains constant
stage closed: pressure rises with increasing temperature

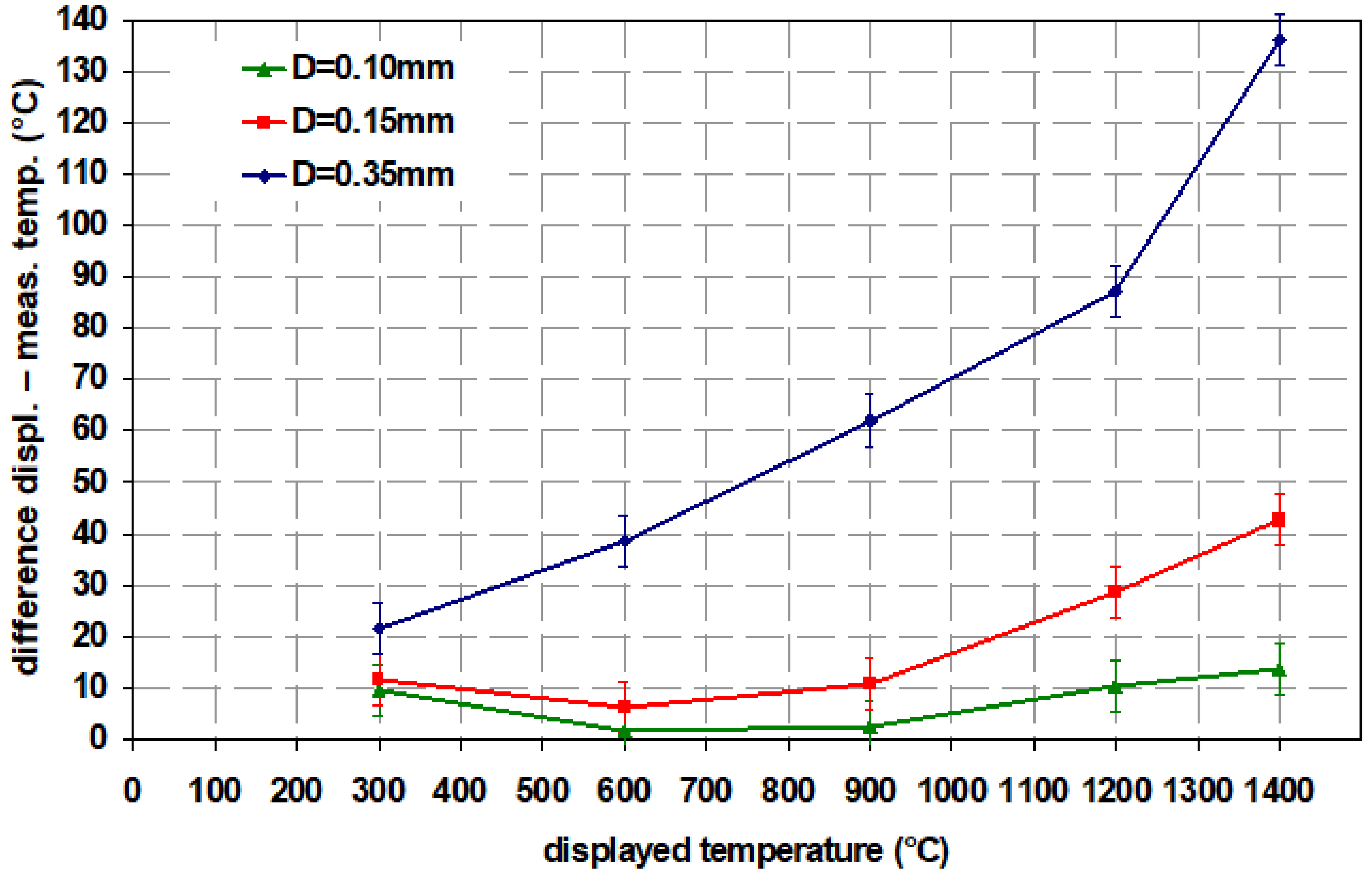
All lattice expansion data from
Touloukian, Y.S., (1977). Thermophysical Properties of Matter, Vol 12&13 Thermal Expansion of Metallic Elements and Alloys & Nonmetallic Solids

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – THERMAL EXPANSION (Al_2O_3 c-AXIS) INFLUENCE OF SAMPLE THICKNESS

Strip Heater (HTK 16N)

› Stage filled with helium
› Three Al_2O_3 samples with thickness of approximately 0.10, 0.15 and 0.35 mm



All lattice expansion data from
Touloukian, Y.S., (1977). Thermophysical Properties of Matter, Vol 12&13 Thermal Expansion of Metallic Elements and Alloys & Nonmetallic Solids

TEMPERATURE VALIDATION

TEMPERATURE VALIDATION – GENERAL STATEMENTS

- An XRD sample stage is not a thermometer. Temperature errors are unavoidable.
- Validation must be done under the same conditions as the measurements (gas type, pressure, sample thickness, ...).
- The validation / reference sample should have similar thermal properties as the sample (color, type of material, ...).
- Validation only makes sense if the temperature deviation is reproducible.
- A good sample stage must provide good reproducibility and minimized absolute deviation.
- Even with good validation and correction, the temperature error will be at least ±2 to ±5 %.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