TGA Calibrations, Adjustments & Maintenance

Queens University Belfast
16/02/12

METTLER TOLEDO

Outline

- Definitions
- Purpose
- References
- Checks
- Manual calibration
- Total calibration
- Flexcal
- Instruction how to calibrate/adjust

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Definitions

Calibration:	Determination of the deviation (Is named „check“ in the method window)
Adjustment:	Change of instrument parameters (Is named „calibration“ in the method window)
Reference substance:	Substance with known approved literature values needed for calibration
Limits of permissible error:	Permissible deviation from desired value

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Selected reference substances

Substance	Temperature [°C]	Enthalpy [J/g]	Effect
Gallium	29.7646	79.88	Melting
Indium	156.5985	28.62	Melting
Tin	231.928	60.4	Melting
Lead	327.46	24.66	Melting
Zinc	419.527	107.5	Melting
Aluminium	660.323	398.1	Melting
Silver	961.9	104.8	Melting
Gold	1064.4	64.5	Melting
Palladium	1554.0	162	Melting
Platinum	1770.0		Melting
Nickel	354.4		Curie
Isatherm	144.5		Curie
Trafoperm	754.3		Curie
Cobalt	1131.0		Curie

Lit.:

H. K. Cammenga et al., Thermochim.Acta 219, 333 – 342, 1993

S. M. Sarge, PTB-Communications 103, 1993

G. Widmann, R. Riesen, Thermal Analysis, 1986

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Calibrations/adjustments for TGA/DSC 1

- Mass
- Furnace temperature with consideration of furnace tau lag
- Sample temperature with consideration of sample tau lag
- Heat flow

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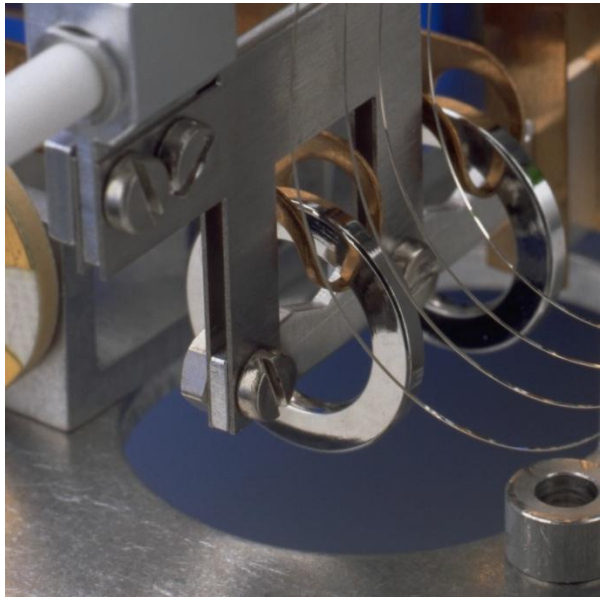
Mass calibration

Internal calibration with two rings (PROFACT not used):

switched off in TGA/DSC1



External calibration with 0.2, 1 and 5 g precision weights (certified).

0.2 g can be used with sample robot for reproducibility check

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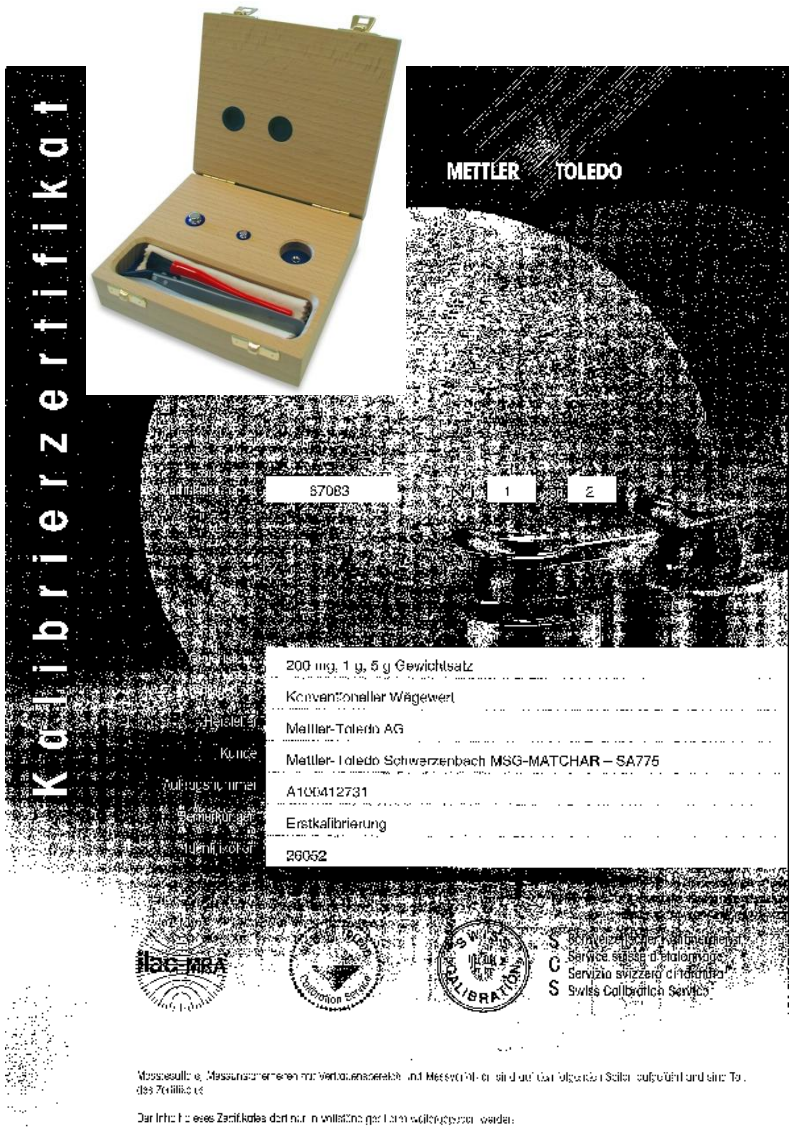
Mass calibration, certificate



Kalibrierzertifikat

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67083 | 1 | 2

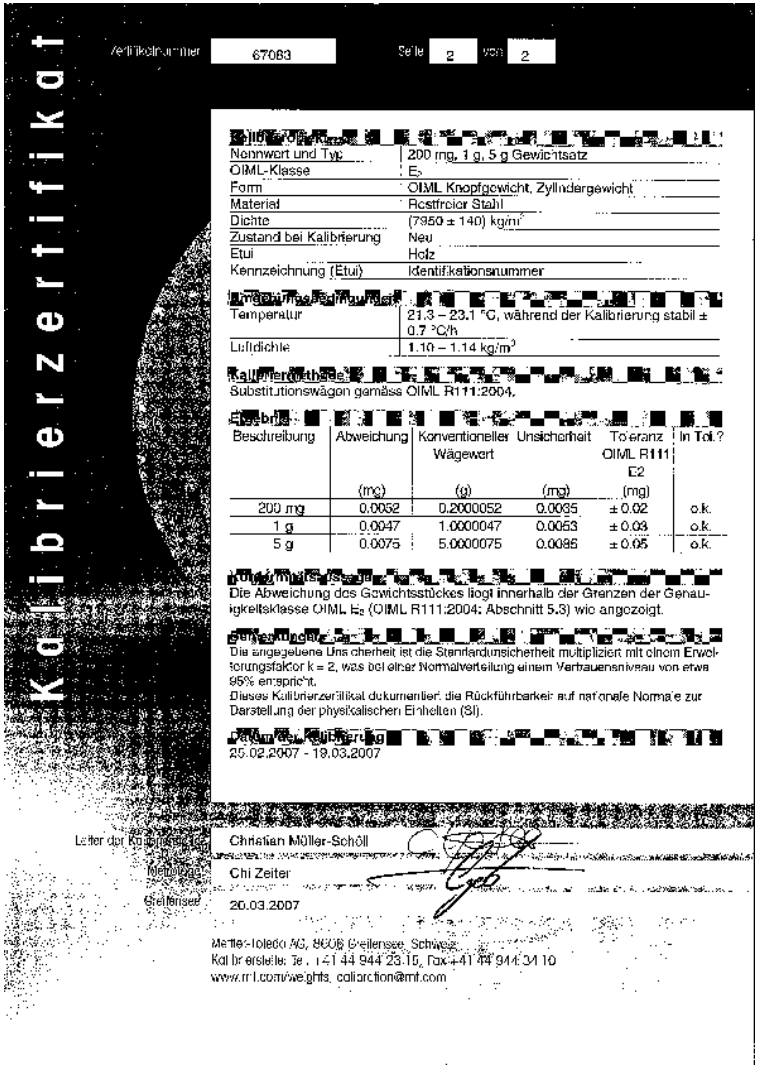
	200 mg, 1 g, 5 g Gewichtsatz
	Konventioneller Wägewert
Hersteller	Mettler-Toledo AG
Kunde	Mettler-Toledo Schwerzenbach MSG-MATCHAR – SA775
Auftragsnummer	A100412731
Kalibrierart	Erstkalibrierung
Kalibrierdatum	26052

ilac-MRA

S Schweizer Kalibrierdienst
C Service suisse d'étalonnage
S Servizio svizzero di taratura
S Swiss Calibration Service

Messabweichungen, Messunsicherheiten mit Verfahrensanweisungen und Messprotokollen sind auf den folgenden Seiten aufgeführt und sind Teil des Kalibrierzertifikates.

Der Inhalt dieses Zertifikates darf nur in vollständiger Form weitergegeben werden.



Kalibrierzertifikat

Zertifikatnummer 67083 Seite 2 von 2

Nennwert und Typ	200 mg, 1 g, 5 g Gewichtsatz
OIML-Klasse	E_2
Form	OIML Knopfgewicht, Zylindergewicht
Material	Rostfreier Stahl
Dichte	(7950 ± 140) kg/m³
Zustand bei Kalibrierung	Neu
Etui	Holz
Kennzeichnung (Etui)	Identifikationsnummer

Umgebungsbedingungen

Temperatur	21.3 – 23.1 °C, während der Kalibrierung stabil ± 0.7 °C/h
Luftdichte	1.10 – 1.14 kg/m³

Kalibrierverfahren

Substitutionswägen gemäss OIML R111:2004.

Ergebnis

Beschreibung	Abweichung (mg)	Konventioneller Wägewert (g)	Unsicherheit (mg)	Toleranz OIML R111 E2 (mg)	In Tol.?
200 mg	0.0052	0.2000052	0.0035	± 0.02	o.k.
1 g	0.0047	1.0000047	0.0053	± 0.03	o.k.
5 g	0.0075	5.0000075	0.0085	± 0.05	o.k.

Bewertung

Die Abweichung des Gewichtsstückes liegt innerhalb der Grenzen der Genauigkeitsklasse OIML E_2 (OIML R111:2004: Abschnitt 5.3) wie angezeigt.

Bemerkungen

Die angegebene Unsicherheit ist die Standardunsicherheit multipliziert mit einem Erweiterungsfaktor k = 2, was bei einer Normalverteilung einem Vertrauensniveau von etwa 95% entspricht.
Dieses Kalibrierzertifikat dokumentiert die Rückführbarkeit auf nationale Normale zur Darstellung der physikalischen Einheiten (SI).

Datum der Kalibrierung

26.02.2007 - 19.03.2007

Leiter der Kalibrierung: Christian Müller-Schöll

Mitarbeiter: Chi Zeiter

Greifensee: 20.03.2007

Mettler-Toledo AG, 8606 Greifensee, Schweiz
Kalibrierstelle: Tel. +41 44 944 23 15, Fax +41 44 944 34 10
www.mt.com/weights, calibration@mt.com

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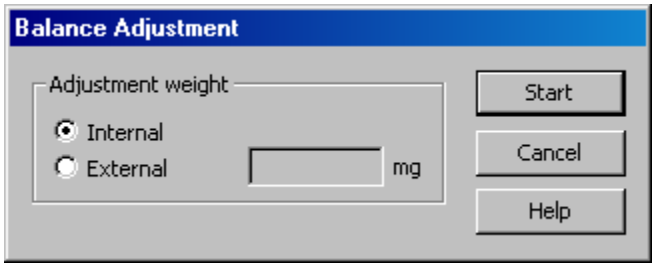
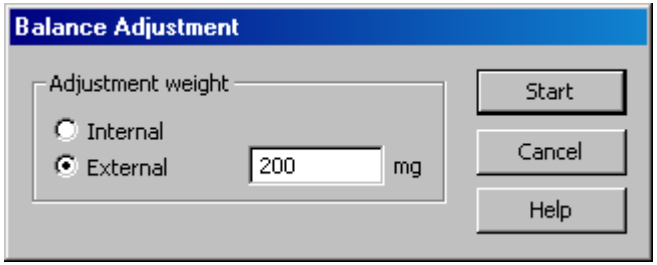
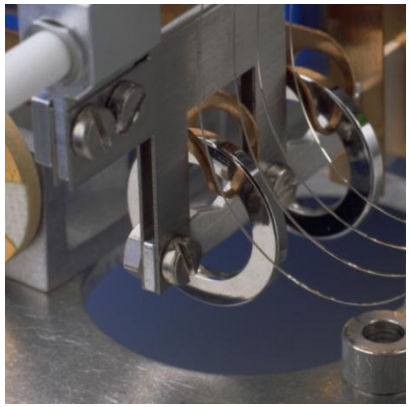
Mass adjustment

Module window, Calib/Adjust, Balance:

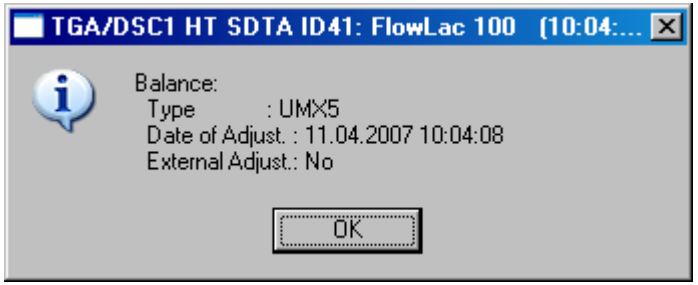
(e.g. adjustment needed when cryostat temperature is changed)







- Using certified masses
- Mind reproducibility
- initial factory adjustment done with sensor



Balance:
Type : UMX5
Date of Adjust. : 11.04.2007 10:04:08
External Adjust.: No

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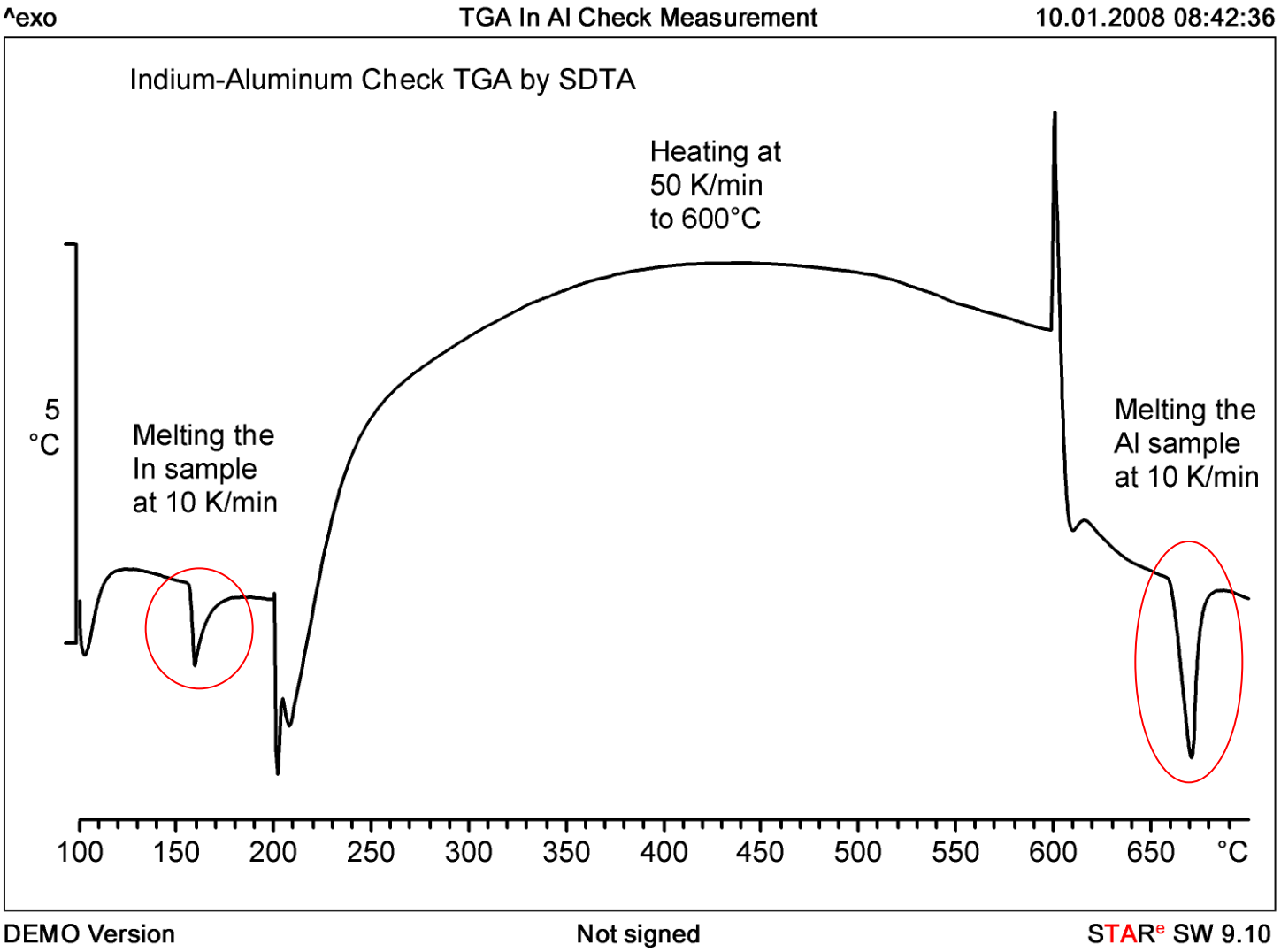
In-Al Check measurement



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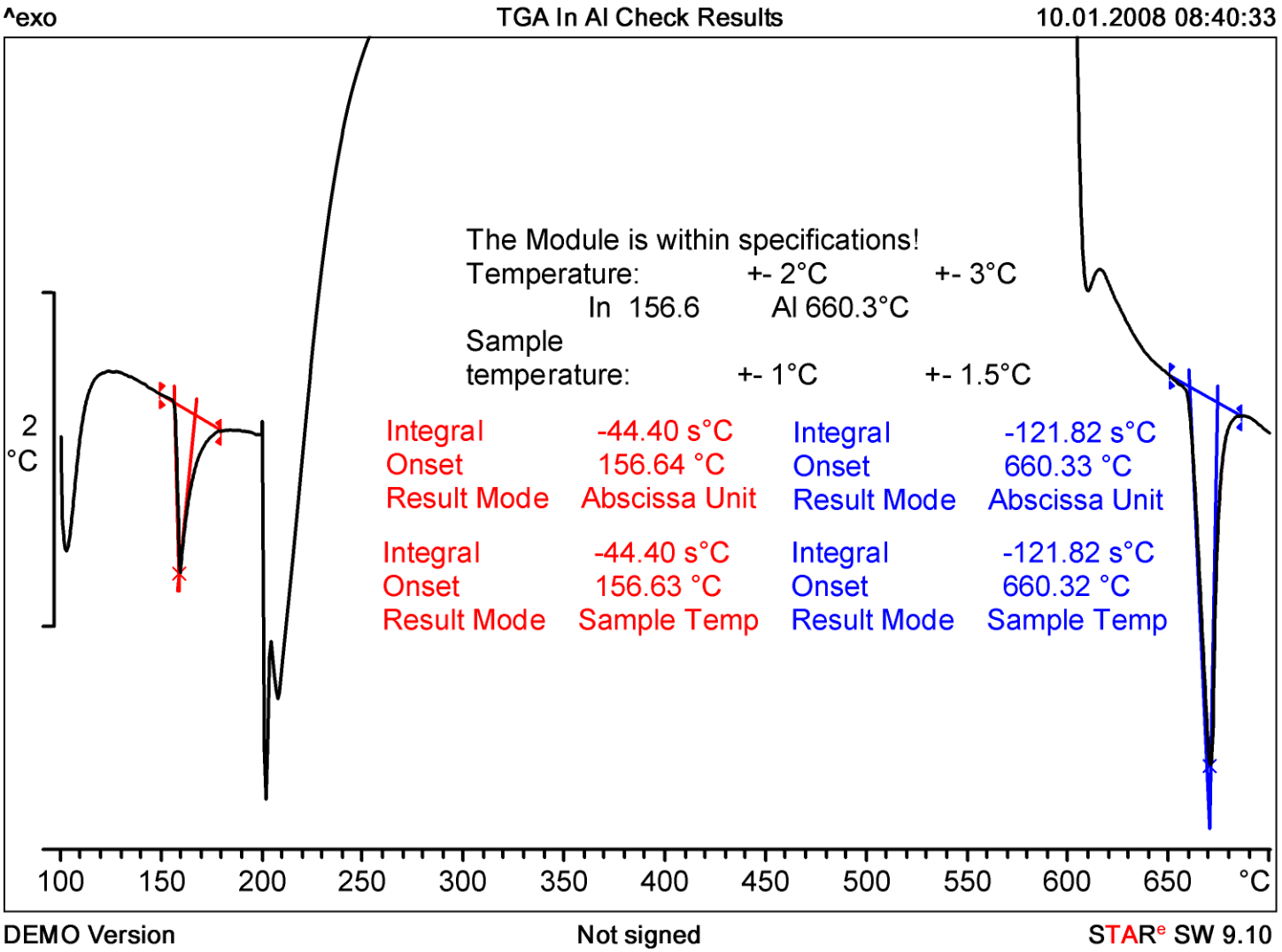
In-Al Check results



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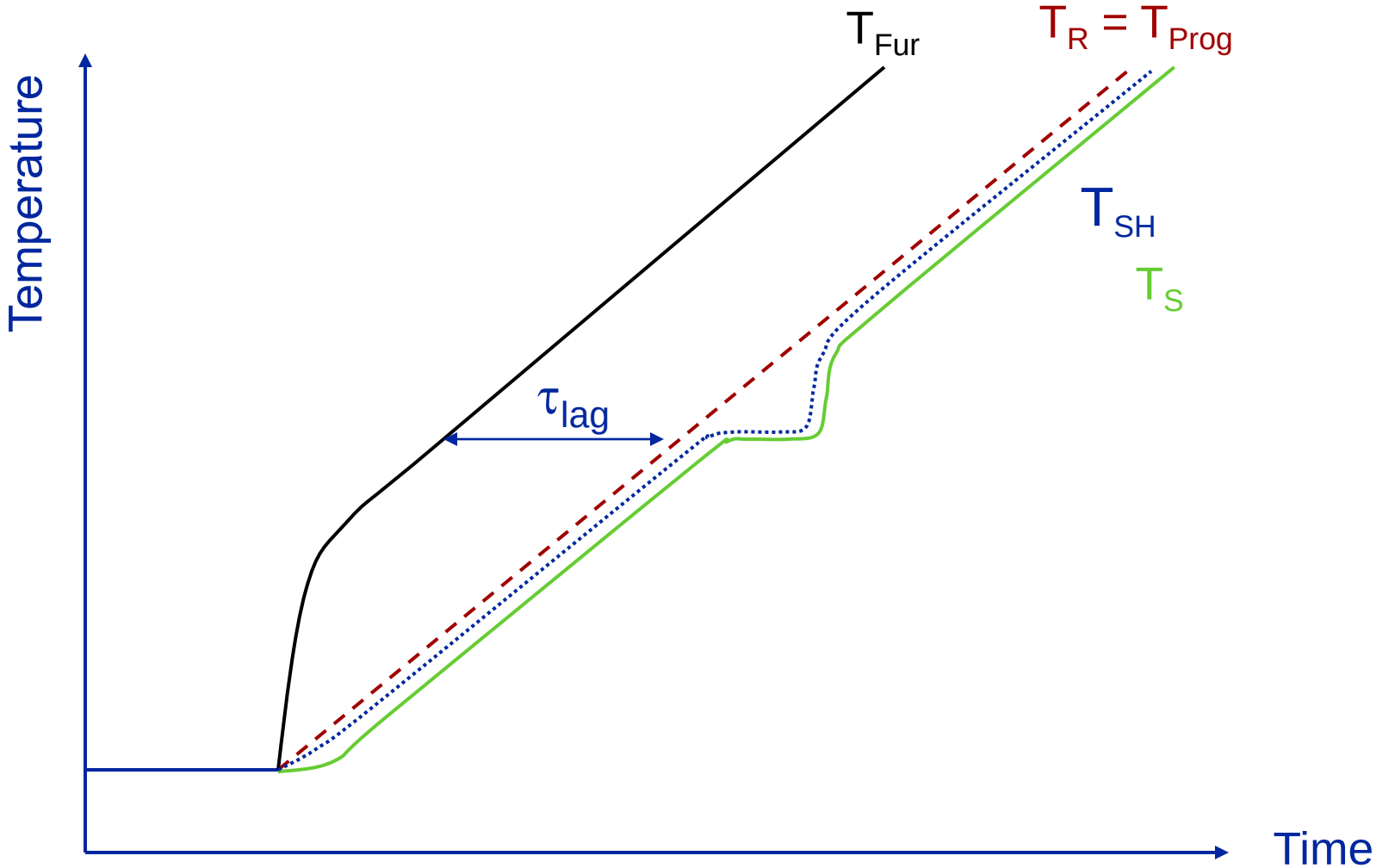
Temperatures in the TGA/DSC 1



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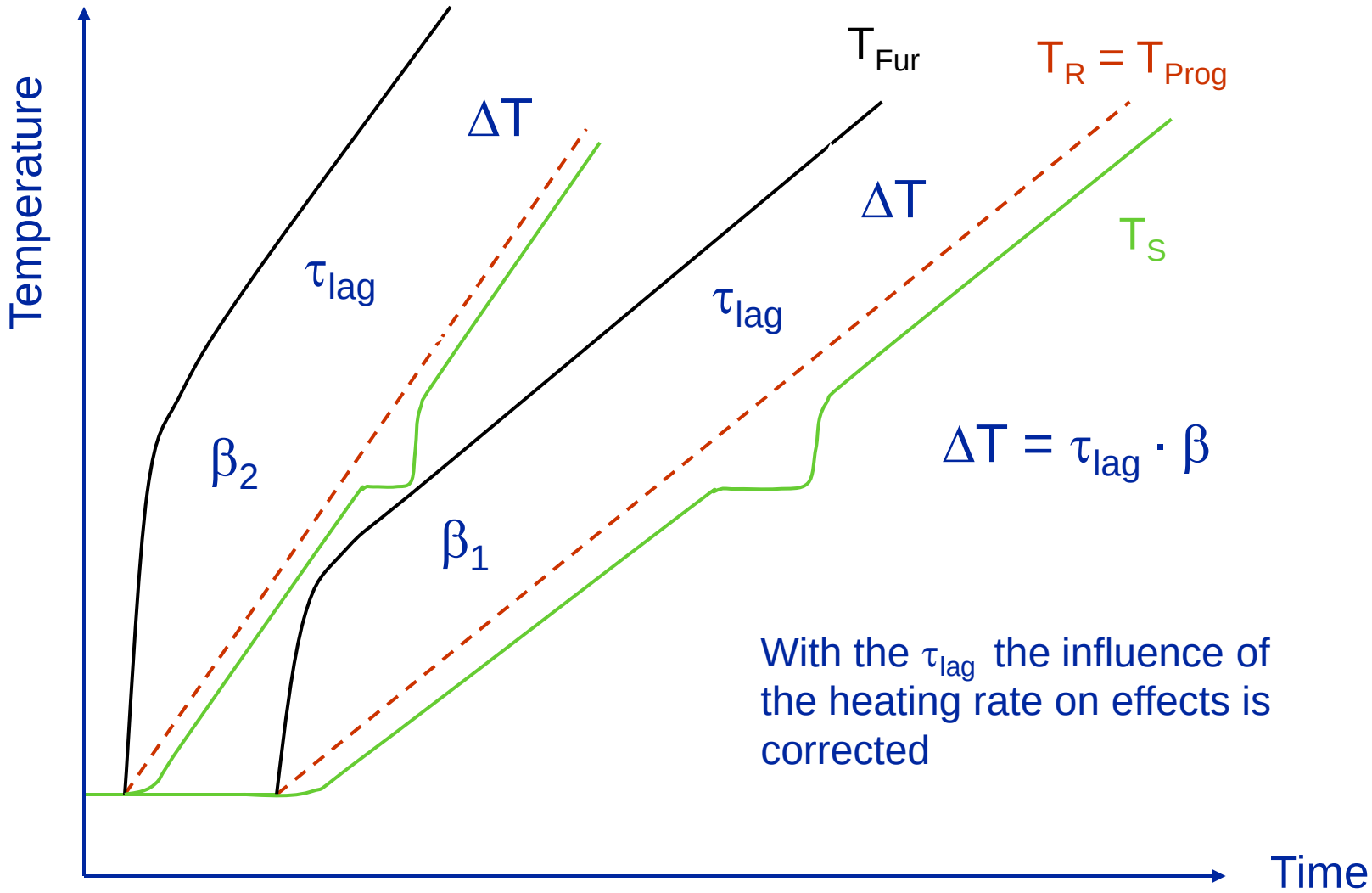
τ-lag calibration



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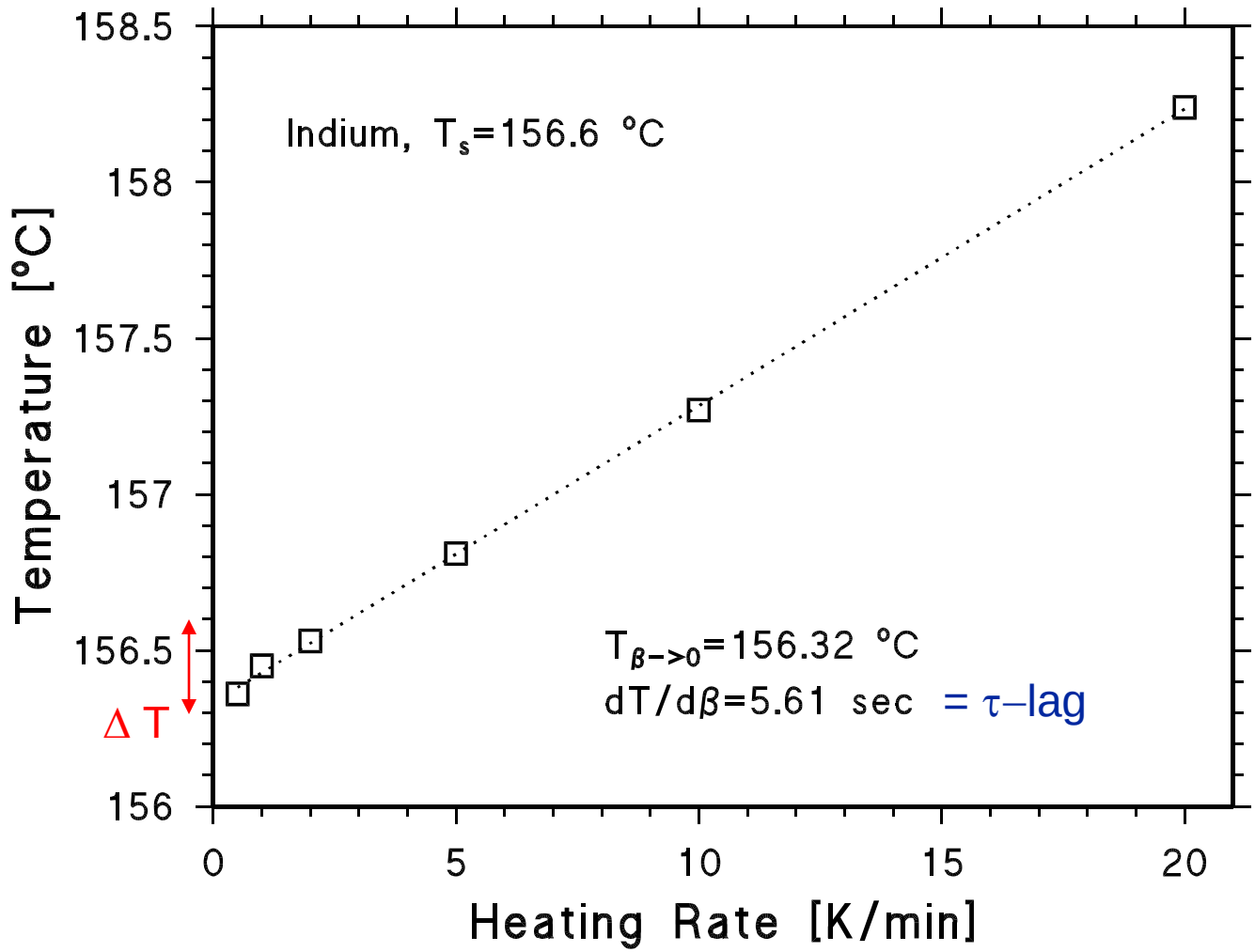
Onset temperature at various heating rates



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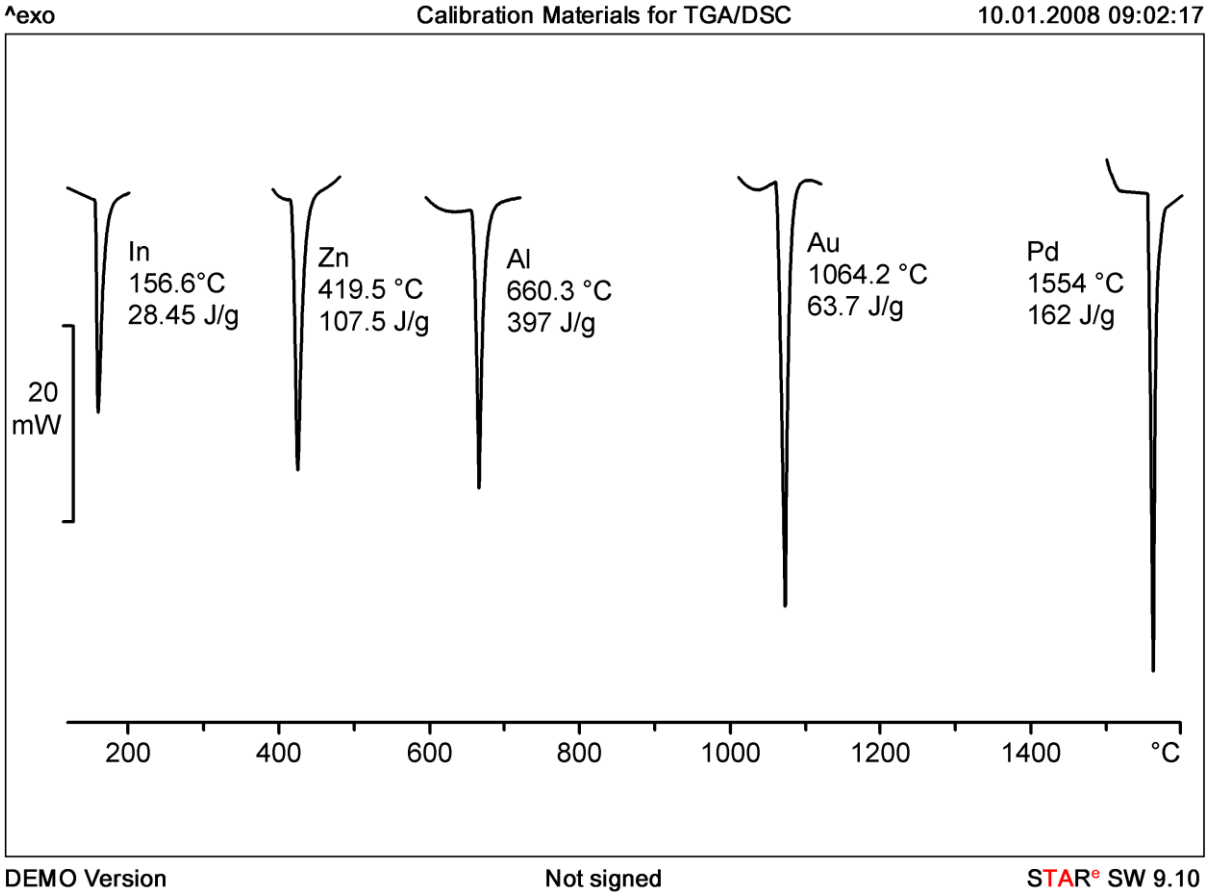
Temperature calibrations



Calibration: melting of pure metals

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Flexcal

The Database takes into account the influence

of different crucibles and purge gases (Tau-Lag-factor):

	Air	Helium	Gas X
70 µl Alox	**4**	2.8	f_x
150 µl Alox	6	4.5	f_x
crucible	f_{air}	f_{He}	f_x

Measurement of the so called „**mother combination**“ delivers a mathematically derived rough calibration for all other combinations.
If other combination is preferred, it should be adjusted separately. In this case no influence on parameters in other cells of the table.

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Temperature adjustment

- There are 2 to 7 relevant thermocouples in the TGA/DSC 1:
- TC in the furnace of all versions → heating rate (reference temperature)
- 1 TC in the SDTA sample holder → SDTA-Signal
- 2 TC in the DTA sample holder → DTA-Signal
- 6 TC in the DSC sample holder → DSC-Signal

- Both sorts of TC have to be calibrated/adjusted with respect to Tau-lag (influence of the heating rate) and the approved literature values.

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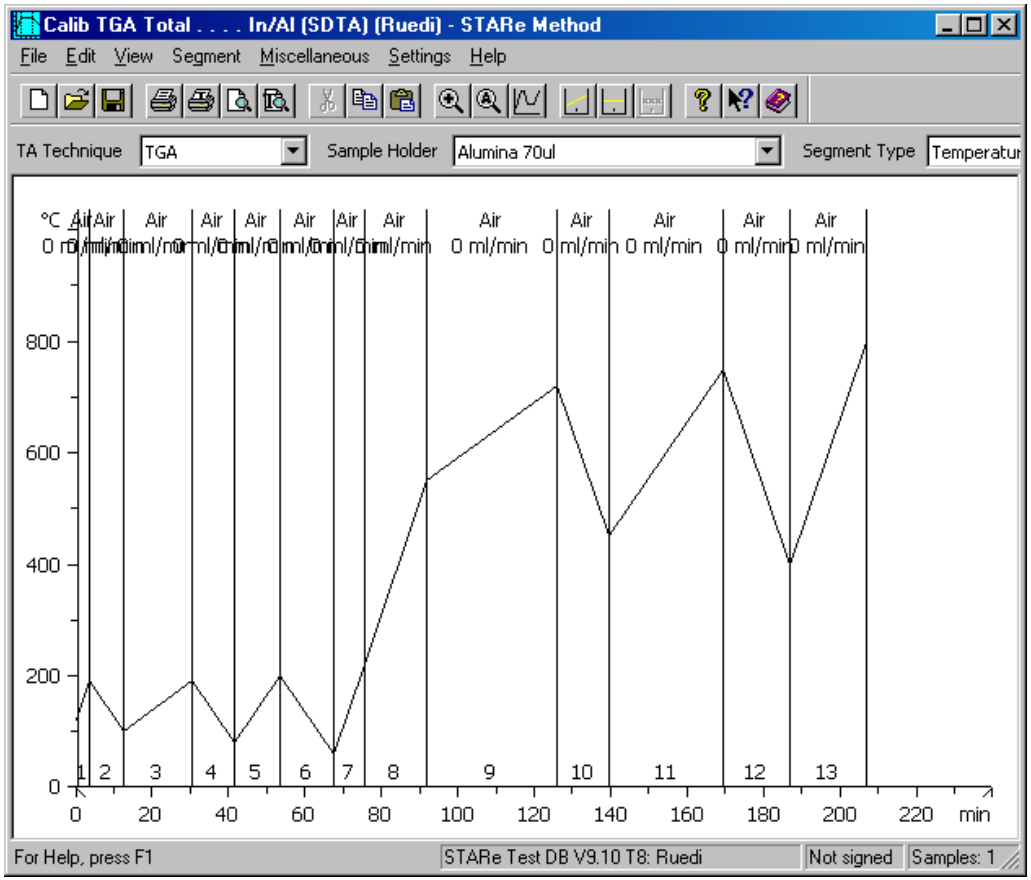
Total Calibration

- For sample and furnace temperature
- For furnace lag and sensor lag
- For **one** point heat flow (In)

- For limited temperature range!
  (max. 520 or 750 °C)
- Do not extrapolate beyond the two temperatures by more than 100 °C.



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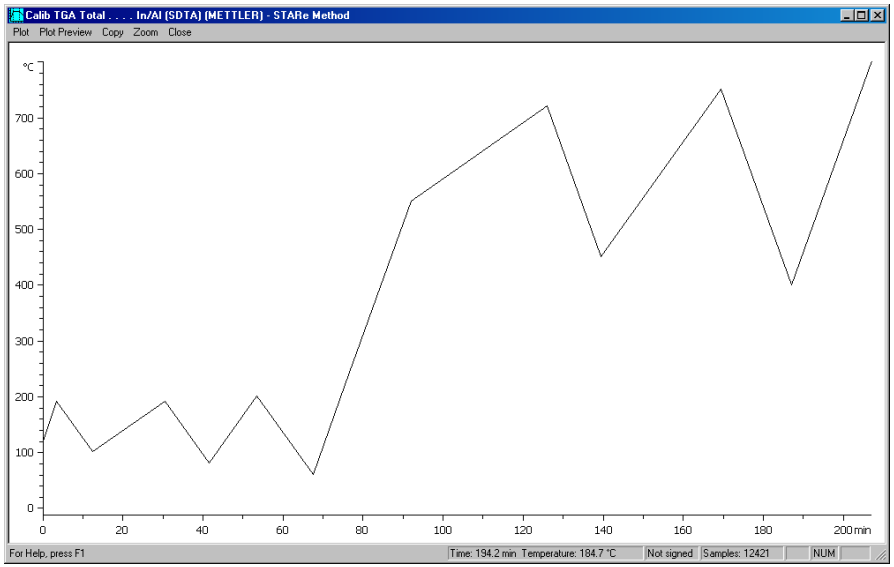
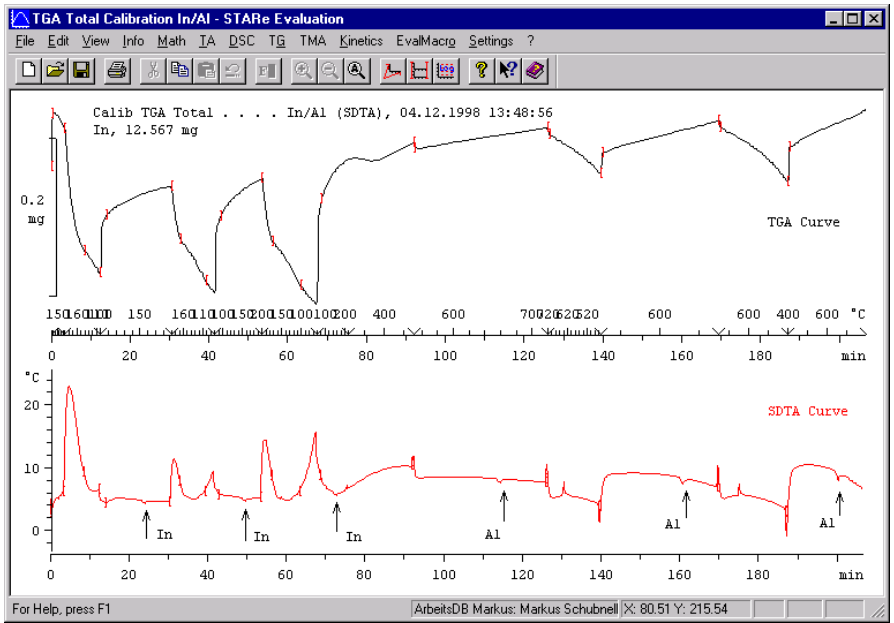
The total calibration





A (Temp)	-14.2127	(-13.4913)	T_f
B (Temp)	14.7804e-03	(16.1765e-03)	
C (Temp)	-14.2130e-06	(-14.2130e-06)	
Deviation	0.76 (25°C)	1.42 (500°C)	
A (Tau Lag)	99.5296	(111.5217)	T_f
B (Tau Lag)	-0.1357	(-0.1400)	
C (Tau Lag)	46.6720e-06	(46.6720e-06)	
Deviation	11.89 (25°C)	9.86 (500°C)	
A (Temp)	3.06	(3.4326)	T_s
B (Temp)	19.1e-03	(26.6702e-03)	
C (Temp)	-17.61e-06	(-17.6100e-06)	
A (Tau Lag)	-0.71	(3.8857)	
B (Tau Lag)	16.14e-03	(53.7905e-03)	
C (Tau Lag)	-14.48e-06	(-14.4762e-06)	

OK Cancel Help

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Editing calibration methods

- Calibration methods can be edited with the method window (demo)
- In case of measurement alloying and loss of material has to be avoided.
- Therefore manual procedures are recommended.

- New reference substances can be added to the database with the help of install plus (demo).

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Manual calibration

Only 1 gas, 1 heating rate, 1 crucible is used (demo):

- Determine the melting points and heats of melting using normal methods and integration evaluations.
- Enter the results manually for temperature, sample temperature and heat flow adjustment (keep other parameters the same!)
- But do not change gas, rate or crucible.

- Make real adjustments for each new pan separately (alumina 70 µl crucible and gas air is already defined = “mother combination”).

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Adjustment by the user

TGA/DSC 1

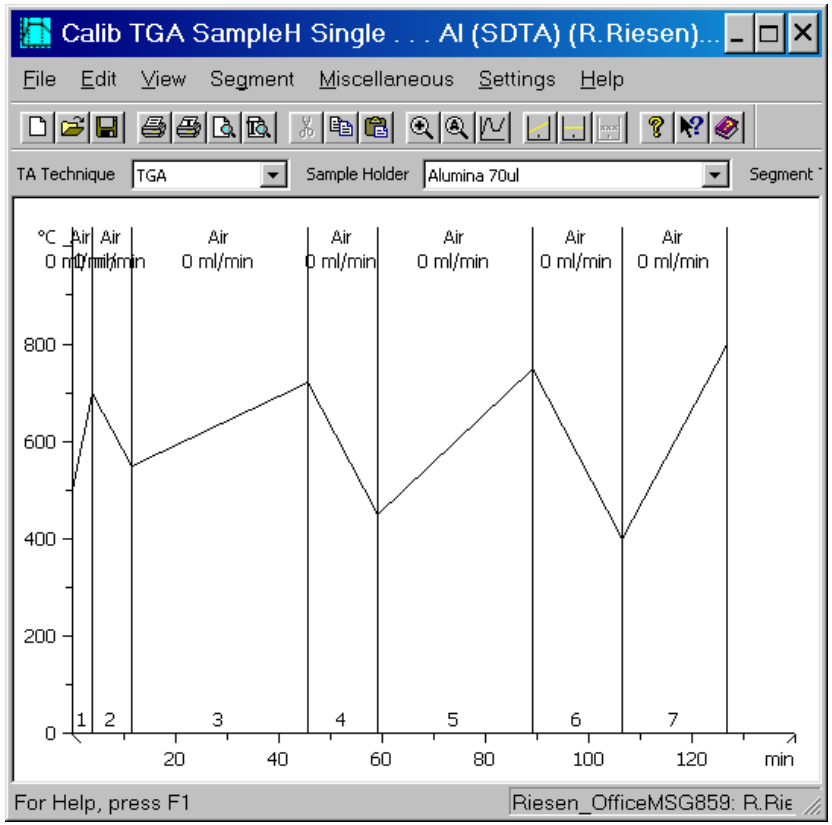
Existing adjustment (calibration) methods can be used only if the following calibration types are selected:

- Temperature single
- Tau lag single
- Heat flow single
- Total
- Sample temperature single, e.g.

  Calib TGA SampleH Single . . . Al (SDTA)

Individual adjustment methods:

Insert temperature <500 °C
Premelt the metals for heat flow
Mind undercooling
Reproducibility



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Individual adjustment

Recommendations:

- Cover the necessary temperature range:
  - small (e.g. 500 °C): use two reference metals (e.g. In and Zn)
  - large (full range): use 4 reference metals (5 for 1600 °C)
- Define the gases and crucibles to be used
- Use single lag program for T_c, τ_{lag}, $T_{s\ and\ lag}$ and heat flow:
  - this enters the respective results in the table for the adjustments
  - no need for manual calculations
- Use the manual Calib/Adjustment functions in the module window

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Manual temperature calibration

- Evaluate the onset temperature of the melting peak with respect to
  - sample temperature and
  - abscissa unit (draw curve versus reference temperature)

  to get the temperatures based on the readings of the two thermocouples.

Remark:
Use "Settings/Result Mode" to switch between the two modes and "Settings /Optional Results/Result Mode" to display the result mode in the result block.

- Enter the readings in the Calibration/Adjustment menu of the module window:
  - To adjust the reference temperature → single temperature
  - To adjust the sample temperature → single sample temperature

Note: in the single sample temperature you also are asked to enter tau-lag values; if you do not have the proper values (this is the usual case !) just enter nothing. In this case, however, **you have to set the new tau-lag values in the next screen back to the old ones!**

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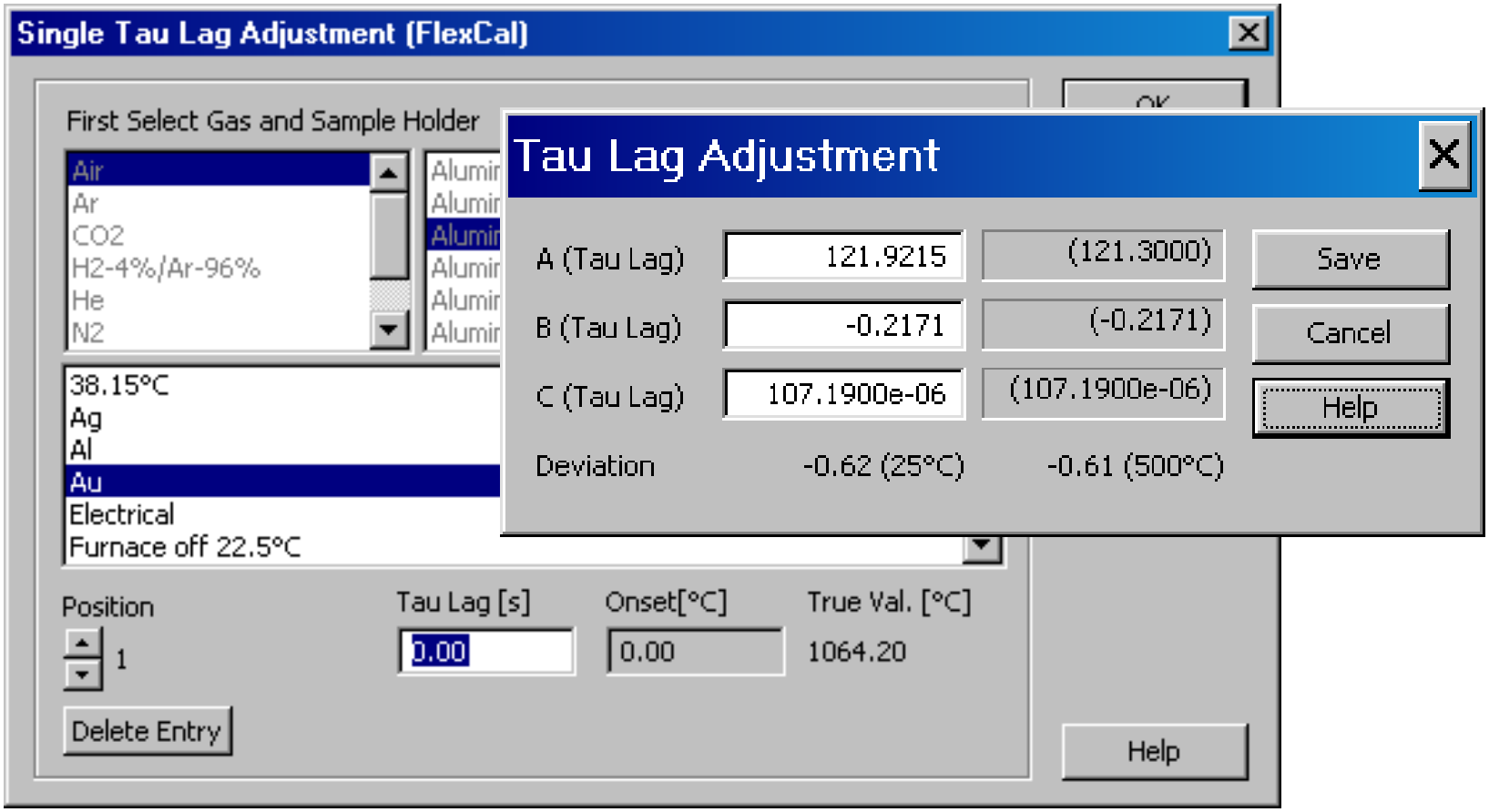
Individual adjustment TGA/DSC 1

- **First step: Furnace lag**

  each sample in an own crucible



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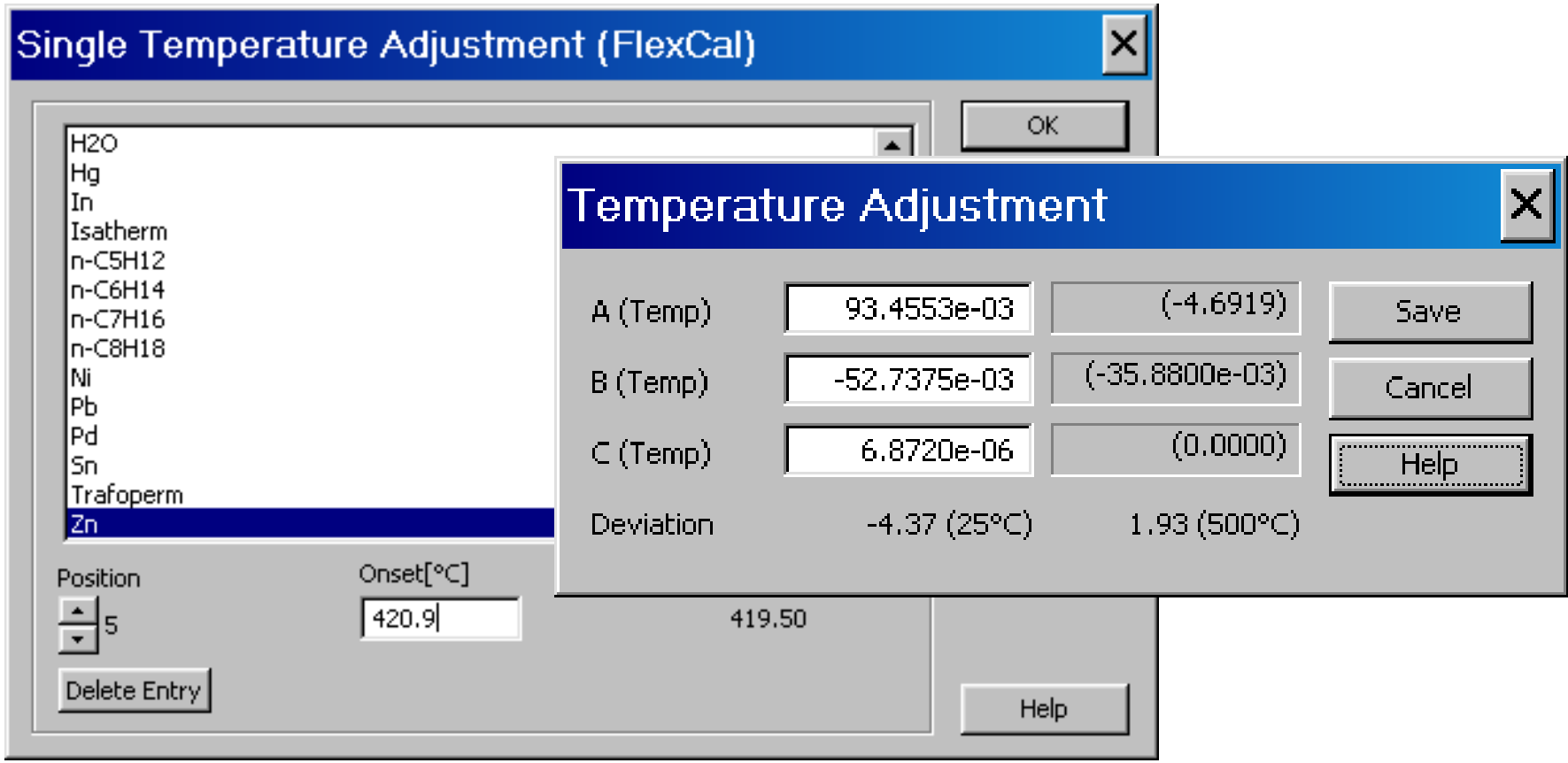
Individual adjustment TGA/DSC 1

- **Second: Furnace temperature**



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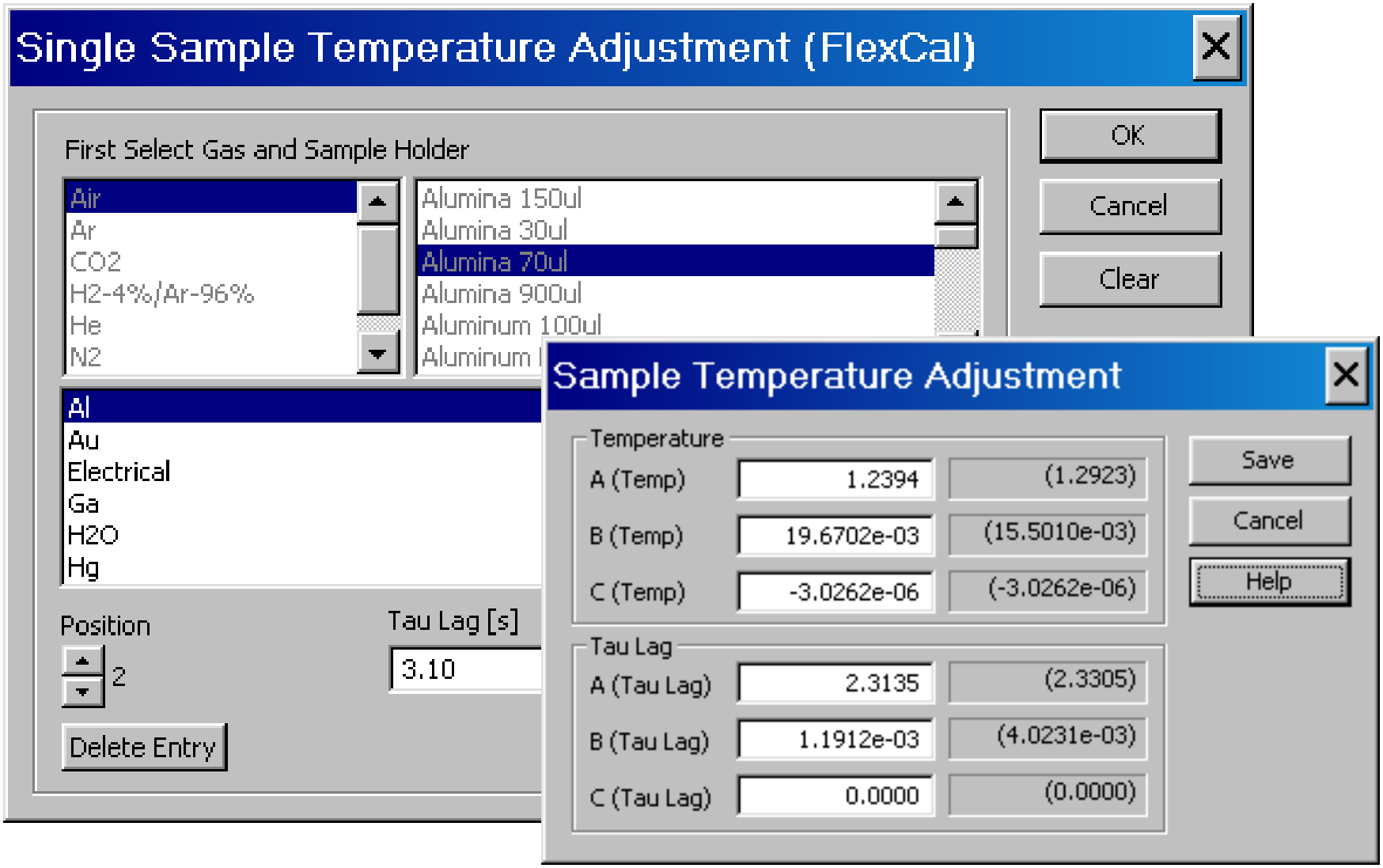
Individual adjustment TGA/DSC 1

- **Third: Sample temperature and lag**



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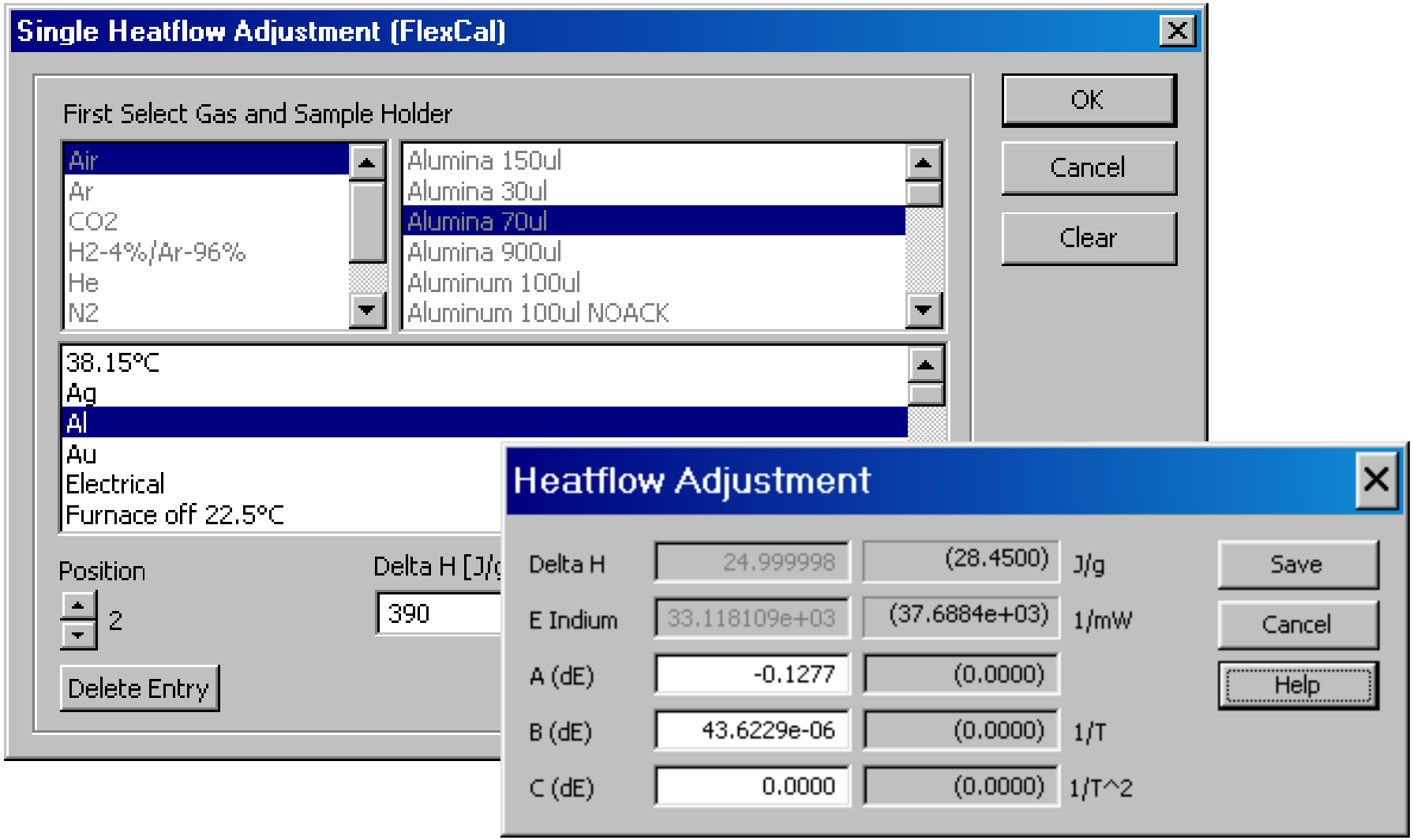
Individual adjustment TGA/DSC 1

- **Forth (last): Heat flow**



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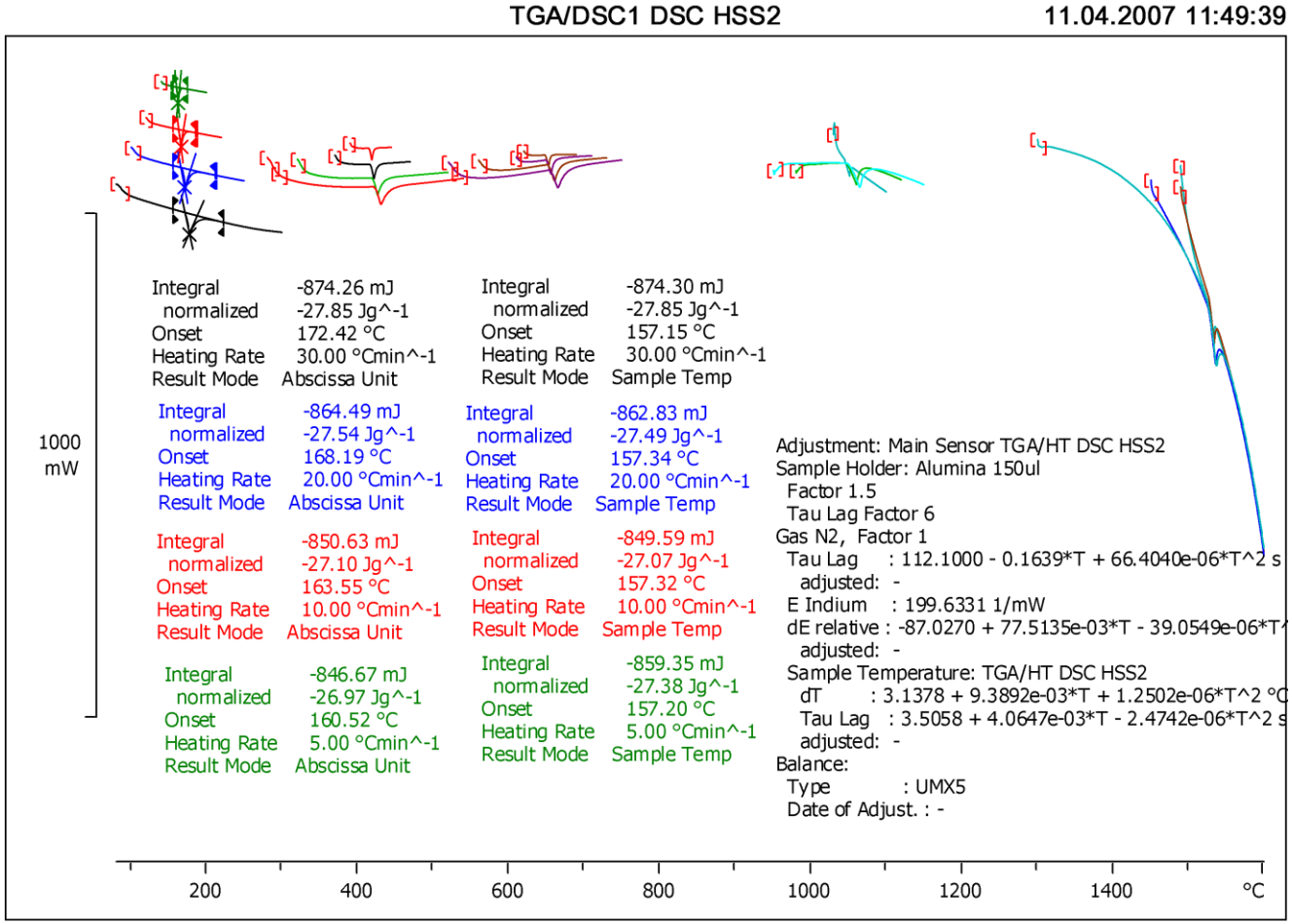
Calibration results

- Results for calculations by special program.
- The new parameters are manually entered in the respective module:

T_c
T_s
τ_{lag}
τ_{sh}
ΔE

all as f(T)



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Module print out

```
Main Sensor:
  TGA/HT SDTA FRS2
  E Nominal:
              a            b            c     Temp.
         16.331    -6.355e-03        0.000    1600.0

Cell Temperature:
  RTyp, adjusted 27.03.2007 16:27:51
  Tc     : 25.00 °C
  dTc(T) : 4.1346 - 0.1673*T - 7.4793e-06*T^2 °C

Model for
 Sample Holder          Alumina 70ul
 Gas                    Air
  Gas Factor    : 1.000000
  Tau Lag       : 98.6080 - 0.1566*T + 69.6870e-06*T^2 s
    adjusted    : -
  Sample Temperature:
    TGA/HT SDTA FRS2, adjusted 27.03.2007 14:57:12
    Tc     : 25.00 °C
    dTs(T) : -0.6371 + 14.9080e-03*T - 4.9680e-06*T^2 °C
    Tau Lag: 0.6111 + 1.8621e-03*T - 1.0544e-06*T^2 s
    E Nominal:
              a            b            c     Temp.
         16.331    -6.355e-03        0.000    1600.0
    dE : 0.0000 + 0.0000*T + 0.0000*T^2 °C
  Heatflow:
    E Indium      : 15.3357 1/mW
    dE relative   : 0.0000 + 0.0000*T + 0.0000*T^2
      adjusted    : -
```

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Results of adjustment for a gas and pan

1. Model for
2. Sample Holder Alumina 70ul
3. Gas Air
4. Gas Factor : 1.000000
5. Tau Lag : 138.4000 - 0.1687*T + 58.8010e-06*T^2 s
6. adjusted : 29.03.2007 17:37:09
7. Sample Temperature:
8. TGA/HT DSC HSS2, adjusted 29.03.2007 17:43:29
9. Tc : 25.00 °C
10. dTs(T) : 3.1378 + 9.3892e-03*T + 1.2502e-06*T^2 °C
11. Tau Lag: 2.0206 + 10.7210e-03*T - 5.5699e-06*T^2 s
12. E Nominal:
13. a b c Temp.
14. 248.290 0.197 -148.580e-06 1600.0
15. dE : -88.1370 + 0.1050*T - 62.5120e-06*T^2 °C
16. Heatflow:
17. E Indium : 202.2450 1/mW
18. dE relative : -88.1370 + 0.1050*T - 62.5120e-06*T^2
19. adjusted : 29.03.2007 17:40:10

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Remarks

Gas factor, Tau Lag Factor:

- Are used if a combination is not adjusted.
  Note: the values are optimized for DSC FRS5 only!
- Without adjustment the “mother calibration” (70 µl alumina, air) is multiplied by:
  - Gas Factor for τ_{lag} of furnace and sensor (T_s)
  - Tau Lag Factor for τ_{lag} of sensor (T_s)
- TGA/DSC 1 Heat flow: factors not active!

Changes of configuration:

- A change of the cell gas type (and sensor) deletes all adjustments!

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How to proceed

- “Warm-up“ of the instrument
- Calibration check (weekly or if any changes at the instrument have been made)
- Check delivers a negative result: check the check
- Instrument needs to be adjusted
- Manual adjustment (use the results of the calibration)
  predefined adjustment procedures:
- Single temperature
  Single Sample holder ‚calibration‘
  Total ‚calibration‘
- Check the new calibration
- The thermocouples may be contaminated by e.g. carbon → heat cleaning
- Blank curves to judge the performance of the balance (noise)

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