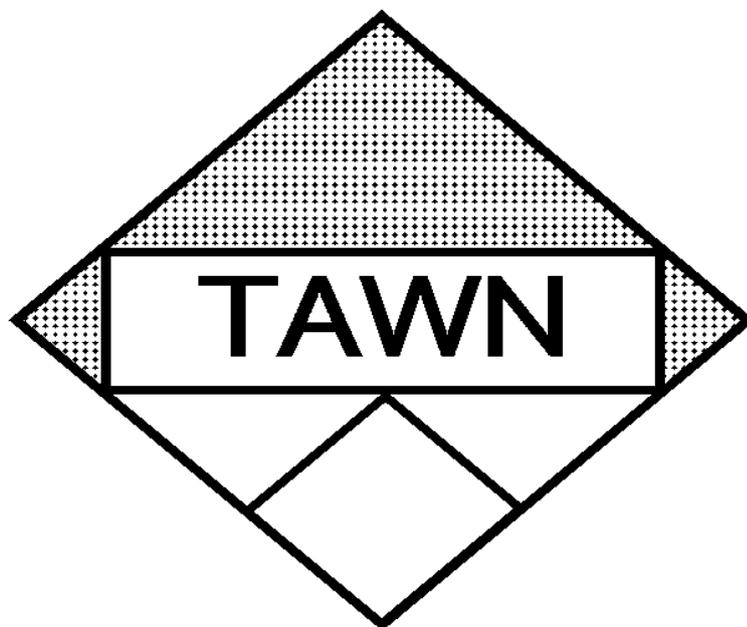


Thermische Analyse Bulletin

Het officiële orgaan van de Thermische Analyse Werkgroep Nederland april 2010



Conferentie data,
ESTAC 2010 , TAD 2010, Apparatuur,
Wetenschappelijke bijdragen, Etc

**Conferentie locatie de Doelen.
22-28 augustus 2010**



WWW.ESTAC10.NL

COLOFON

Het Thermische Analyse Bulletin is het officiële orgaan van de Thermische Analyse Werkgroep Nederland (TAWN). Het bulletin wordt gratis aan de leden gestuurd.

In het bulletin worden opgenomen:

- nieuws van het bestuur van de werkgroep;
- gegevens over congressen, symposia en cursussen;
- internationaal nieuws;
- boekbesprekingen;
- gegevens over nieuwe apparatuur en de toepassing ervan.

Redactie:

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De TAWN stelt zich niet verantwoordelijk voor enige onjuistheden of fouten en de gevolgen daaruit voortvloeiende. Tevens is zij noch de redactie verantwoordelijk voor de inhoud van ingezonden stukken.

REDACTIONEEL

Het uitbrengen van het Bulletin heeft ernstige vertraging opgelopen door gebrek aan bijdragen. Bovendien was nog geen informatie beschikbaar over de ESTAC 10 en de te organiseren cursus. De PATON die de theoretische TA cursus organiseert is inmiddels failliet verklaard. Vandaar dat het bestuur toch dit jaar nog een praktische cursus wil organiseren, welke bij TNO wordt gehouden. Hier is ook voor het eerst de mogelijkheid voor TGA. Allen die aan deze cursus willen deelnemen moeten dit zo spoedig mogelijk bij de voorzitter of secretaris kenbaar maken. Verder wordt iedereen opgeroepen om actief aan de ESTAC 10 deel te nemen en op tijd in te schrijven.



Bestuur TAWN

Dr. P.J. van Ekeren, voorzitter

Ing W.P.C. de Klerk, secretaris

**Ir. A.J. Witteveen,
penningmeester**

**Dr. Ir. G. Hakvoort,
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contacten**

**Prof. Dr. G.R.J. van den
Mooter**

**M.F.J. Pijpers, redacteur
bulletin**

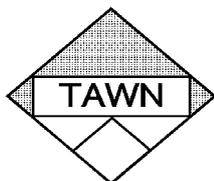
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Inhoudsopgave

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THERMISCHE ANALYSE WERKGROEP NEDERLAND

Sinds 1965 bestaat er in Nederland een werkgroep (vanaf 1990 een officiële vereniging) genaamd Thermische Analyse Werkgroep Nederland, afgekort TAWN. Deze werkgroep heeft thans bijna 300 leden, die zich vanuit zeer verschillende onderzoeksgebieden bedienen van thermische analyse (DTA, DSC, TG, TMA, DMA, etc.) en calorimetrische technieken. De TAWN is lid van de internationale organisatie op het gebied van thermische analyse en calorimetrie, de ICTAC (International Confederation for Thermal Analysis and Calorimetry).

Doel van de TAWN

Het doel van de werkgroep is het bevorderen en verspreiden van kennis en kunde op het gebied van thermische analyse en calorimetrie. Om dit doel te bereiken worden er activiteiten georganiseerd, waar de leden onderling informatie kunnen uitwisselen met betrekking tot de mogelijkheden van thermische analyse en calorimetrie bij fundamenteel en toegepast onderzoek alsmede bij kwaliteitscontrole van producten.

Activiteiten

Jaarlijks wordt een thermische analysedag (TAD) georganiseerd. Daarnaast zijn er thema(mid)dagen over speciale onderwerpen. Tijdens deze bijeenkomsten houden leden of uitgenodigde sprekers voordrachten over hun werk. De toegang is voor leden gratis. Deze bijeenkomsten bieden uitstekende mogelijkheden om contacten op te bouwen met andere onderzoekers in hetzelfde vakgebied.

Daarnaast werkt de TAWN intensief mee aan cursussen op het gebied van de thermische analyse en calorimetrie.

Een aantal maal per jaar geeft de werkgroep een blad uit, het Thermische Analyse Bulletin. Dit blad wordt gratis naar de leden gestuurd.

LIDMAATSCHAP

Het lidmaatschap van de TAWN is slechts mogelijk voor natuurlijke personen; de contributie bedraagt

€ 10,- per jaar. Opgave is mogelijk door de ingevulde aanmeldingsstrook te zenden naar de secretaris van de vereniging.

Sponsoring

Voor bedrijven en instellingen bestaat de mogelijkheid de werkgroep te sponsoren. Ook kunnen advertenties worden geplaatst in het TA-bulletin. Informatie hierover is verkrijgbaar bij de secretaris van de werkgroep of de redacteur van het TA-bulletin.

Aanmelding als lid van de TAWN

Ondergetekende geeft zich op als lid van de TAWN.

Naam: _____ Hr./Mw. Titel(s): _____ Voorletters: _____

Bedrijf/Instelling: _____

Afdeling: _____

Adres: _____

Postcode en Plaats: _____

Telefoon: _____ Fax: _____ E-mail: _____

Handtekening: _____

Deze strook sturen naar de secretaris van de TAWN:

Ing. W.P. C. de Klerk
TNO-Defence, Safety and Security, location Rijswijk
BU3 - Protection, Munitions and Weapons
Department Energetic Materials
(Lifetime studies & Microcalorimetry)
P.O. box 45
2280 AA Rijswijk
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e-mail : wim.deklerk@tno.nl



**U KUNT NOG STEEDS AAN HET BESTUUR DE
BEHOEFTE KENBAAR MAKEN VOOR EEN
THERMISCHE ANALYSE CURCUS: DSC OF TGA.
ZIE PAGINA 11**



Jaarverslag (periode: 28 november 2008 tot 24 november 2009)

Dames en heren,

Op de gebruikelijke wijze informeer ik u over de ontwikkelingen die plaatsvonden in de periode tussen de Thermische Analyse Dag in 2008 en die in 2009. Een aantal elementen, waaronder de financiële verantwoording over het boekjaar 2008, komen later in deze ledenvergadering uitgebreid aan de orde.

De daling van het aantal leden heeft zich ook het afgelopen jaar doorgezet. Op dit moment hebben we 167 leden. We hebben de leveranciers van thermische analyse apparatuur gevraagd om ons te helpen TA-gebruikers te wijzen op het bestaan van de TAWN. Het is verheugend dat zij allen bereid zijn om hieraan mee te werken. TA Instruments heeft in een uitgebreide e-mailing onze folder verspreid. Dat was succesvol en heeft een aantal nieuwe leden opgeleverd. Mogelijk hebben ook de andere bedrijven al actie ondernomen.

Het bestuur heeft zich in de verslagperiode bezig gehouden met de volgende zaken.

- Vorig jaar hebben we voor het eerst een "Reisbeurs voor Jonge Onderzoekers" kunnen uitreiken. Dit jaar hebben we getracht om een sponsor voor deze beurs te vinden. Dat is helaas niet gelukt, ongetwijfeld mede door de economische situatie. Ook is er dit jaar helaas geen aanvraag voor een reisbeurs ontvangen. Graag wijzen wij u nogmaals op deze mogelijkheid; mocht u in uw omgeving geschikte kandidaten kennen, informeer hen dan.
- Het bestuur heeft gesproken over de mogelijkheid TAWN-cursus "DSC-cursus met nadruk op praktische handelingen" weer te organiseren. Er is echter minder bereidheid bij apparatuurleveranciers om op dezelfde wijze medewerking te verlenen. We overwegen nu om de cursus op een andere wijze te organiseren bij TNO.
- In 2010 wordt in Nederland het internationale congres ESTAC-10 (in De Doelen te Rotterdam) georganiseerd. Dit heeft de constante aandacht van het bestuur. Later in deze vergadering zult u wat uitgebreider worden geïnformeerd.

Graag wil ik van deze gelegenheid gebruik maken om de sponsors van de vereniging te bedanken. Dat waren afgelopen jaar de werkgevers van de bestuursleden, die het mogelijk maken dat de bestuurstaken voor een belangrijk deel in werktijd kunnen worden uitgevoerd (KU Leuven, TNO Defensie en Veiligheid), Ankersmid voor de sponsoring van de TAD-2008 en ESA/ESTEC voor de sponsoring van deze TAD-2009. Alle sponsors, evenals de adverteerders in het TA-Bulletin, worden heel hartelijk bedankt.

Ik dank u voor uw aandacht en ik hoop u op een volgende activiteit weer te mogen begroeten.

Kascontrole commissie

Beste leden,

Zoals afgesproken op de TAWN ledenvergadering van november 2008 zouden wij U via het ledenbulletin berichten over de controle van de boekhouding van de vereniging. Dit zou nog 2009 hebben plaatsgevonden, maar kon door omstandigheden helaas niet doorgaan. Vandaar dat wij op 5 februari j.l. bij dhr Witteveen thuis zijn geweest ter controle van de boeken van 2008. Bij deze berichten wij de leden dat er geen onvolkomenheden zijn geconstateerd in de boekhouding van de vereniging en dat wij de penningmeester, dhr Witteveen, in deze decharge verlenen over de boekhouding van 2008, welke door ons beide is ondertekend.

Tevens hebben wij ook de afgeronde boekhouding van 2009 gecontroleerd, maar daarover berichten we U uiteraard op de ledenvergadering van 2010.

Met vriendelijke groet namens de kascontrole commissie

René Hoekstra
Ko Schaap

FINANCIEEL JAAROVERZICHT TAWN 2009 (IN EURO)

Inkomsten

Uitgaven

Contributies	1560,00	Bestuur	758,60
Advertenties	150,00	Vereniging	422,71
Rente			
Rentemeerrekening	532,10	TAD'08 (spreker)	634,06
		TA-Bulletin	657,58
		Negatief saldo	-230,85
Totaal	2242,10	Totaal	2242,10

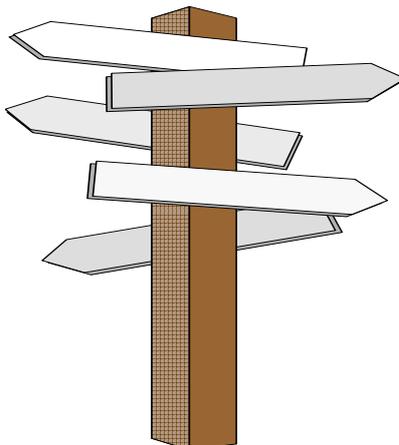
Saldi (per 31.12.2008)

Saldi (per 31.12.2009)

Giro	286,64	Giro	23,69
Rentemeerrekening	18398,71	Rentemeerrekening	18430,81
Totaal	18685,35	Totaal	18454,50

**Adri Witteveen,
01.01.2010**

CONGRESSEN, SYMPOSIA, CURSUSSEN



7th Heat Flow Calorimetry Symposium
Rijswijk, NL, 17.05 - 20.05.2010

wim.deklerk@tno.nl

13th International Symposium on Loss Prevention and Safety Promotion in the Process Industries

Brugge, B, 06.06. - 09.06.2010

<https://www.ti.kviv.be/conf/Lossprevention2010/>
info@lossprevention2010.com

ESTAC-10 (10th European Symposium on Thermal Analysis and Calorimetry)
Rotterdam, NL, 22.08. - 27.08.2010

NATAS 38th Annual Conference August 15 – 18, 2010 Houston Hall
University of Pennsylvania

11th Lähnwitzseminar on Calorimetry 2010 in Rostock
June 6, evening until June 11, morning

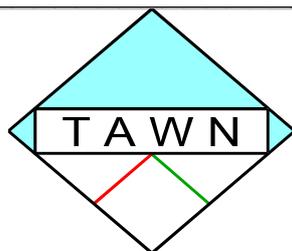
Joint International Symposium on Temperature, Humidity, Moisture and Thermal Measurements in Industry and Science:

[TEMPMEKO & ISHM 2010, 31.05. -04.06.2010](#)

<http://www.tempmeko-ishm.org/>

European Conference on Thermophysical Properties:

[ECTP 19, 2011, Thessaloniki, Griekenland](#)



Cursus Thermische Analyse met nadruk op praktische handelingen

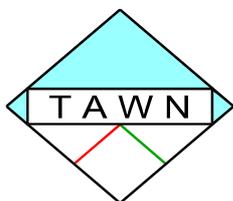
Wij zijn voornemens om in oktober 2010 een nieuwe cursus Thermische Analyse met nadruk op praktische handelingen te organiseren.

In 2005 werd voor het laatst de uiterst succesvolle cursus "DSC-cursus met nadruk op praktische handelingen" georganiseerd. Geregeld krijgen wij vragen of er binnenkort weer een cursus wordt gegeven zodat het erop lijkt dat er weer voldoende belangstelling is om binnenkort weer een cursus te organiseren.

Het is waarschijnlijk dat de opzet van de cursus iets zal wijzigen ten opzichte van de eerder gegeven cursussen. Mogelijk zal naast DSC ook TGA worden behandeld. Wat in ieder geval blijft is dat het een onafhankelijke cursus is waarbij korte theoretische inleidingen worden gevolgd door het in groepjes uitvoeren van thermische analyse experimenten en het interpreteren van de meetcurven.

De cursus zal 2 à 3 dagen duren, hoogstwaarschijnlijk in ergens in oktober.

Belangstellenden worden verzocht om contact op te nemen met Paul van Ekeren, voorzitter TAWN (e-mail: Paul.vanEkeren@tno.nl; tel. 015-2843280).



Reglement Reisbeurzen voor Jonge Onderzoekers

1. Om het oordeelkundig gebruik van Thermische Analyse en/of Calorimetrie in Nederland en Vlaanderen te stimuleren kan het bestuur van de TAWN een beurs toekennen aan jonge onderzoekers die op een (inter)nationaal congres of symposium resultaten van hun werk willen presenteren door middel van een lezing of een poster.
2. Het bestuur van de TAWN zal zich inzetten om deze mogelijkheid bekend te maken.

3. Het te presenteren werk moet voor een significant deel bestaan uit het correct toepassen van Thermische Analyse, zoals DSC, DTA, TG, TMA, DMA en DEA, of calorimetrie.
4. Het budget dat voor de beurzen beschikbaar is wordt door het bestuur van de TAWN vastgesteld. Het bestuur zal trachten om het budget via één of meer sponsors bijeen te brengen.
5. De frequentie van toekenning van beurzen is budgetgebonden, en daardoor mede afhankelijk van de sponsormiddelen. In principe wordt gestreefd naar een jaarlijkse toekenning van een beurs.
6. Een beurs kan op ieder gewenst tijdstip worden toegekend aan een kandidaat die een aanvraag indient bij het bestuur. De aanvraag dient te zijn voorzien van een 'abstract' van de presentatie, aangevuld met relevante informatie om de aanvraag te kunnen beoordelen. Tevens dient een begroting van de kosten te worden overlegd.
7. De kandidaat voor een beurs dient de leeftijd van 35 jaar nog niet te hebben bereikt.
8. Over toekenning van een beurs wordt beslist door het bestuur van de TAWN op basis van de kwaliteit van de voorgestelde presentatie.
9. Wanneer een bestuurslid zelf is betrokken bij het werk van een kandidaat, dan zal hij wel mee kunnen overleggen en adviseren, maar niet deelnemen aan een eventuele stemming over toekenning van een beurs.
10. De beurs bestaat uit een geldbedrag. De hoogte van dit bedrag wordt bepaald door het bestuur, maar zal nimmer meer bedragen dan het totaal van de inschrijvings-, reis- en verblijfskosten.
11. In geval van sponsoring worden de sponsors vermeld bij de uitreiking van de beurs en bij de presentatie.
12. Van degene die een beurs krijgt toegewezen wordt verwacht dat hij/zij een voordracht zal houden over zijn/haar werk tijdens een door de TAWN georganiseerde Thermische Analyse bijeenkomst in Nederland of Vlaanderen.
13. Een persoon kan slechts eenmalig een beurs ontvangen.
14. Het TAWN-bestuur is niet gebonden opening van zaken te geven over de besluitvorming.
15. In gevallen waarin dit reglement niet voorziet beslist het TAWN-bestuur.

Vastgesteld te Utrecht,
in de TAWN-bestuursvergadering op 21 september 2006.

**OPROEP VOOR SPONSORING EN HET BESCHIKBAAR
STELLEN VAN EEN LOKATIE VOOR DE TAD IN
NOVEMBER 2010.**

**Volgende nu volgende artikelen zij bijdragen van firma's en
vallen buiten de verantwoordelijkheid van de redactie.**

Persbericht:

Linseis vertegenwoordiging naar Ankersmid

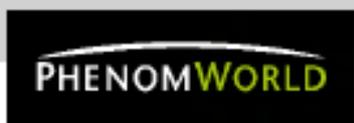
LINSEIS levert al ruim 50 jaar innovatieve producten voor thermische analyses en ter bepaling van thermofysische parameters. De bepaling van deze fysische parameters sluit naadloos aan op de expertise en focus binnen Ankersmid. Ankersmid en Linseis bundelen krachten in de Benelux en bieden daarmee een compleet pakket aan instrumenten, aangevuld met technische support en applicatie kennis.

We bieden hiermee een serie instrumenten voor R&D en QC, bestaande uit DSC – Differential Scanning Calorimeter, TGA - Thermogravimetry, STA – Simultaneous Thermal Analysis, TMA – Thermomechanical Analysis, DIL - dilatometer, Laser Flash – Xenon Flash Thermal Conductivity / Thermal Diffusivity Analyzer en evolved gas analysis met FTIR en massa spectrometer.

Linseis streeft ernaar om voorop te lopen in het ontwikkelen van nieuwe technieken en analysers om wensen en eisen van onze klanten in te vullen. Gecombineerd met de hoge kwaliteit van de producten geniet Linseis van een uitstekende reputatie onder wetenschappelijke instituten en gevestigde industrie.

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**TA Instruments – BNL
2010 Training Schedule**

We would like to invite you to the TA Instruments training courses for Thermal Analysis, Microcalorimetry and Rheology. These courses are a mix between theory and hands-on. Everyone with interest in these techniques is welcome to attend.

Module	Date
DSC Training Course (theoretical)	9 – 10 February (B) 1 – 2 June (NL) 16 – 17 November (B)
DSC Training Course (practical)	30 March (B) 9 September (NL)
MDSC Training Course (theoretical)	9 March (B) 25 November (NL)
MDSC Training Course (practical)	18 May (B)
TGA Training Course (theoretical)	31 March (B)
TGA Training Course (practical)	13 October (B)
DMA Training Course	21-22 April (B) 28-29 September (B)
Universal Analysis (software)	12 October (B)
Rheology Training Course (basic)	17-18 March (B) 12-13 October (NL)
Rheology Training Course (advanced theory)	2-3 March (B)
Sorption Analysis Training Course	19 May (Manchester – UK) 14 July (London – UK)
Microcalorimetry Training Course (TAM III, TAM Air, nanoDSC, nanoITC)	16-18 February (Germany) 23-25 March (Sweden) 28-30 September (Germany) 12-14 October (Sweden)

Location for the training: TA Instruments application laboratories in Zellik (B) or Etten-Leur (NL) unless otherwise mentioned. Course language is English.

Our Annual Benelux User Meeting 2010 is scheduled October 27-28.

TA Instruments is present at “Het Instrument” in Amsterdam (September 28-October 1).

More information?

- available at the Benelux pages of our website www.tainstruments.com
 - contact Nadia Rassart, phone (+32) 02 706 00 80 or (+31) 076 508 72 70
 - mail to belgium@tainstruments.com or netherlands@tainstruments.com
-

Resolve
SOLUTIONS BY ANALYSIS



DSM 

Geert Vanden Poel/Albert Sargsyan/Vincent Mathot

**Towards a DIN Specification for Temperature Calibration
of Fast-Scan Calorimeters (FSC)ⁱ**

1. Calibration of Fast-Scan Calorimeters

The calibration of Fast-Scan Calorimeters (FSC) is more complicated than the calibration of a Standard DSC. However, for both techniques the *first step* is the primary calibration. The latter consists of calibrating the temperature, then heat flow and finally the furnace.

The *second step* is the sample mass calibration using primary or secondary standards. This step is used to study the influence of the sample mass and the heating rate on the extrapolated onset temperature and the peak temperature, and to finally build the correction matrices for these temperatures. The extrapolated onset temperature and the peak temperature are defined in Figure 1. Note the difference between extrapolated onset temperature and real onset temperature, which latter temperature corresponds to the beginning of the melting of the substance. The extrapolated onset temperature is used because the real onset is not trivial to determine, while it also depends on the purity of the sample.

The *third step* is to check the symmetry of the FSC's using secondary standards. Symmetry means that the correction factors applied in heating can

also be applied in cooling. Each of these steps will be explainedⁱⁱ in detail in the following sections.

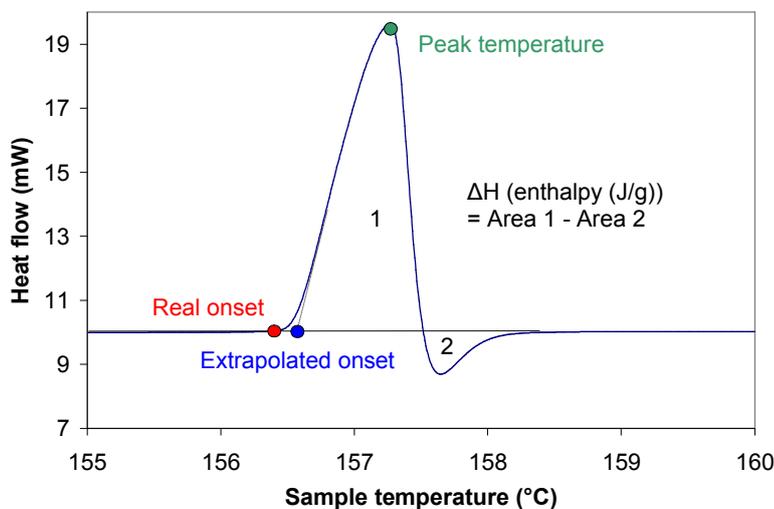


Figure 1: Definition of the extrapolated onset temperature and the real onset temperature from the heat flow rate curve.

Before performing the calibration, the inert purge gas has to be chosen. The calibration is dependent on many parameters including the gas atmosphere: helium; a He/Ne mixture, here consisting of 10% helium and 90% neon; nitrogen etc.

1.1. Primary calibration

The temperature calibration consists of measuring the extrapolated onset temperatures of the calibration standards and then to equal these to their respective literature values. A check of the temperature calibration has to be made after the temperature-, the heat flow- and the furnace (only for PerkinElmer DSC) calibration, in order to confirm that these calibrations were successful.

Standards like indium, tin, zinc (which are primary standards), adamantane, benzophenone can be used to calibrate the temperature behavior of FSC's in the heating mode over a wide temperature range of -150 to 350 °C.

The sample masses of these primary calibration standards are to be chosen in between 1 ± 0.1 mg with an applied heating rate, S_h , of 10 °C/min.

A heating rate of 10 °C/min is chosen because this scan rate is widely used in the thermal analysis community, and surely by the industrial users. A zero

heating rate as recommended by GEFTA is considered to be scientifically interesting but, for the present purpose, a second choice [1]. Moreover, it is felt that the results of extrapolation to zero heating rate are still disputable, because the way of extrapolation is not unequivocal. The sample mass of 1 mg is chosen because samples having such mass are easy to handle and are very well detectable by FSC's even for slow cooling and heating rates.

Figure 2 represents the result of the temperature calibration using the phase transition temperatures of the calibration substances listed in Table I. In this example Adamantane, benzophenone, indium and tin were used. For each standard, the extrapolated onset temperature was determined, and in addition the enthalpy of melting for indium to verify the heat flow calibration. The literature value for the enthalpy of melting of indium as provided by PerkinElmer is 28.45 J/g and for comparison, the measured enthalpy was 28.44 J/g for HPer DSC Pyris 1 and 28.40 J/g for HPer DSC Diamond.

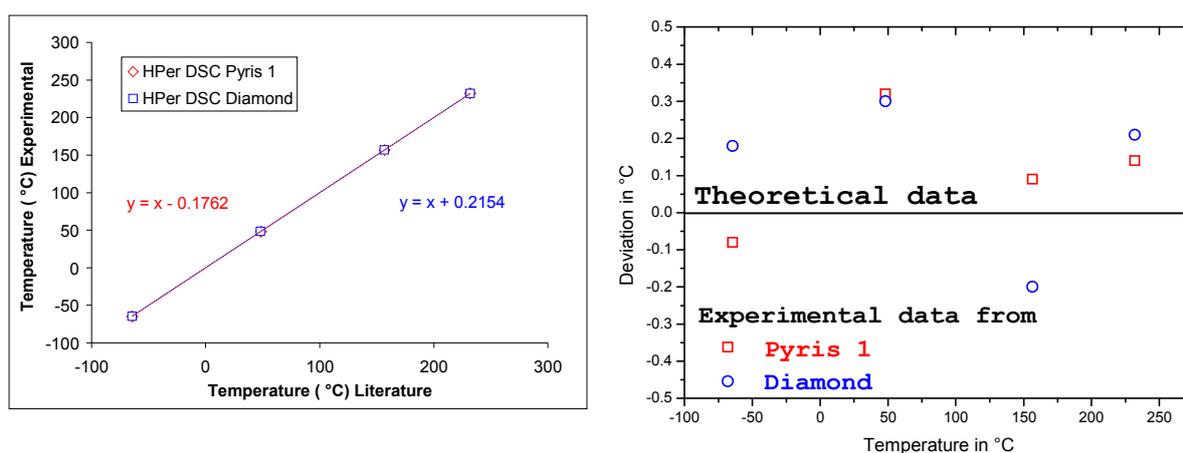


Figure 2: Result of the primary calibration of FSC's and deviation plot.

Surprisingly, in literature, the values measured and recommended for the enthalpy of melting of indium scatter appreciably. Therefore, the best route is to verify the heat flow calibration by way of a heat capacity measurement on Sapphire, which is the most suitable standard for heat capacity calibration. However, because in practice this is not feasible for the thermal analysis & calorimetry users, the present protocol does not take such a procedure into accountⁱⁱ.

ⁱ. Nevertheless, it would be interesting and useful if a participant would perform both ways of calibration

Concerning the temperature calibration, the data in Figure 2 were fitted by a linear regression (left side), while the quality of the fit is presented by the deviation plot (right side). Statistical process control (SPC) could be an effective method of monitoring the calibration process, enabling objective criteria for the quality arrived at.

Table I: Substances used for temperature calibration in heating mode.

Substance	Evaluation	Type of transition	Phase transition temperature	
			(literature) (°C)	(K)
adamantane	TEO	Solid-solid	-64.53	208.62
benzophenon	TEO	Solid-liquid	48.10	321.25
indium	TEO	Solid-liquid	156.60	429.75
tin	TEO	Solid-liquid	231.93	505.08

1.2. Sample mass calibration

After primary calibration, a sample mass calibration has to be performed. Therefore, several indium samples are weighed with masses between 0.1 mg and 10 mg. In order to reduce the influence of the sample container, aluminum foil of about 3 mg is used for wrapping the sample, which way of packaging also provides an improved (3D) heat conductivity path to the sample. The samples were subjected to heating rates from 1 to 500 °C/min. The extrapolated onset temperatures and the peak temperatures have been measured in order to build up correction matrices [ii].

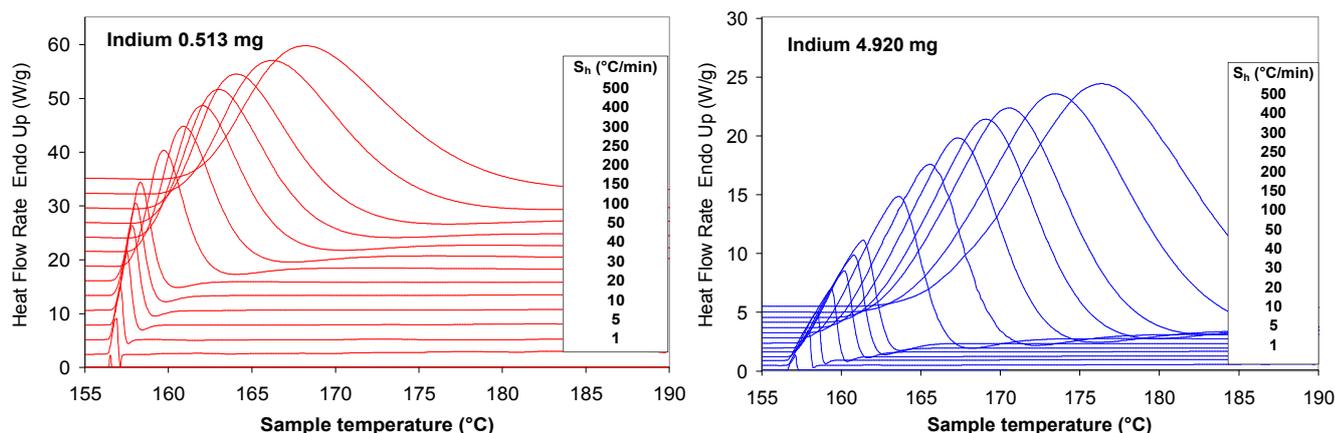


Figure 3: Heat flow rate curves obtained for indium samples for various heating rates.

Figure 3 shows the obtained heat flow rates of indium samples at different heating rates and sample masses. For each heating rate, the extrapolated onset temperature and the peak temperature are calculated (Figure 4). Figure 4 presents the influence of the heating rate and of the sample mass on the extrapolated onset temperature and on the peak temperature for FSC's, in this particular case the PerkinElmer HPer DSC Diamond. The temperature onset is highly influenced by the sample mass and the heating rate. The peak temperature is influenced by the sample mass and the heating rate as well.

These deviations are due to the thermal lag, which is linked to the heat transfer from the heating system to the sample. Therefore, it is recommended to reduce the sample and crucible mass to reduce the thermal lag, minimizing the correction factors.

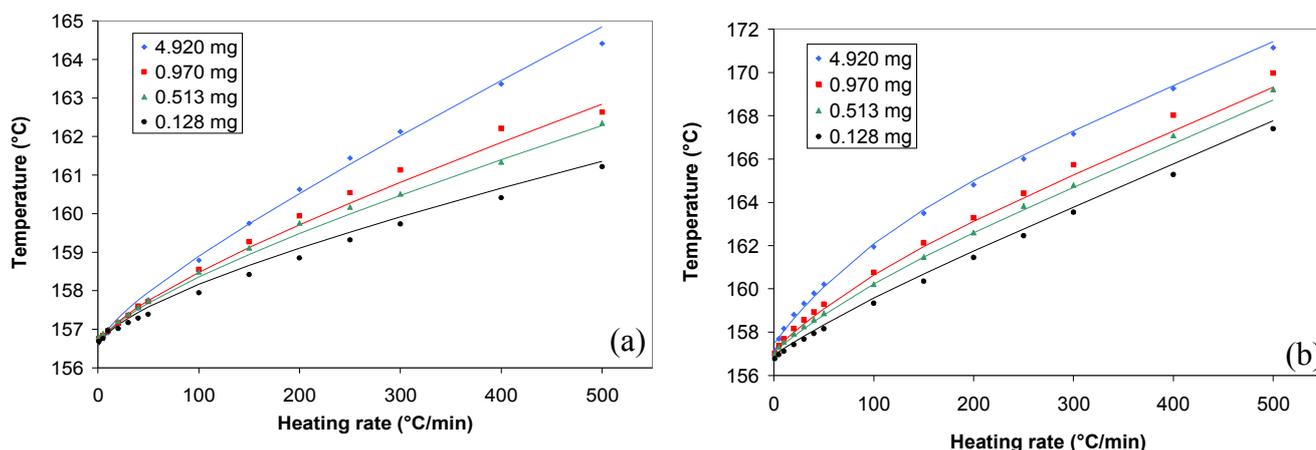


Figure 4: The influence of the sample mass and heating rate on (a) the extrapolated onset temperature and (b) the peak temperature for indium.

For the present protocol both K (e.g. K/min; K/s) and °C (e.g. °C/min; °C/s) can be used ^[2]. However, for the figures representing DSC data the use of °C is preferred *throughout*: for the temperature axis, for scan rate, and in expressions like J/g°C. The reasons are twofold: it provides uniformity of the results (a mixed use of °C and K should be avoided) and the majority of the users – including all of industry – prefer the use of °C.

² In the document "The International System of Units (SI)", 8th edition (2006), which is the English translation of the official French text of the Bureau International des Poids et Mesures, it is stated explicitly in section [2.2.2.5](#): "*A difference or interval of temperature may be expressed in kelvins or in degrees Celsius (13th CGPM, 1967/68, Resolution 3, mentioned above), the numerical value of the temperature difference being the same*". The authors interpret this as allowing the use of both K (e.g. K/min; K/s) and °C (e.g. °C/min; °C/s)

1.3. Fitting

In order to build up the correction matrices, mathematical fitting is applied using 'grey-box' formulae for the extrapolated onset and peak temperatures.

The experimental data on *extrapolated onset temperatures* have been fitted using the following formula (1):

$$T_{EO}(S_h, m) = a_0 + a_1 S_h^{a_2} + (a_3 S_h + a_4) m^{a_5} \quad (1)$$

with $T_{EO}(S_h, m)$: extrapolated onset temperature, S_h : heating rate ($^{\circ}\text{C}/\text{min}$), m : sample mass (mg), $a_0 = 155.7006$; $a_1 = 0.129946$; $a_2 = 0.483677$; $a_3 = 0.007762$; $a_4 = 0.18$; $a_5 = 0.212784$.

The experimental data on *peak temperatures* have been fitted using the following formula (2):

$$T_P(S_h, m) = a'_0 + a'_1 S_h^{a'_2} + (a'_3 + a'_4 e^{a'_5 S_h}) m^{a'_6} \quad (2)$$

with $T_P(S_h, m)$: peak temperature, S_h : heating rate ($^{\circ}\text{C}/\text{min}$), m : sample mass (mg), $a'_0 = 156.7062$; $a'_1 = 0.01068$; $a'_2 = 1.08766$; $a'_3 = 3.4426$; $a'_4 = -2.97$; $a'_5 = -0.00998$; $a'_6 = 0.299$.

1.4. Correction matrices

Correction matrices for extrapolated onset temperature

A correction factor for extrapolated onset temperature is defined based on the reference onset temperature of indium melting as follows:

$$CF_{T,EO} \equiv T_{EO,ref} - T_{EO}(S_h, m) \quad (3)$$

with $T_{EO,ref} = 156.60$ $^{\circ}\text{C}$ for the primary standard indium of mass 1 mg and heated at 10 $^{\circ}\text{C}/\text{min}$. Table II gives an example of the correction factors found for the extrapolated onset temperatures, calculated by means of formula (3), as based on the fit using formula (1).

Correction matrices for the peak temperature

A correction factor is calculated based on the reference peak temperature of indium.

The correction factor for the peak temperature is defined as:

$$CF_{T,P} \equiv T_{P,ref} - T_P(S_h, m) \quad (4)$$

with $T_{P,ref} = 157.6$ °C for the primary standard indium of mass 1 mg and heated at 10 °C/min. This value has to be confirmed to be a constant value by the abovementioned SPC method. Furthermore, this so-called peak temperature will vary with the type of FSC. As an example, Table III presents the correction factors for the peak temperatures, calculated by applying formula (4), as based on the fit using formula (2).

The symmetry check must be performed to ensure that these correction matrices can also be used in the cooling mode.

Table II: Correction matrix for the determination of the correction factors for HPer DSC Diamond.

Sh (°C/min)	Correction factor for the extrapolated onset:			
	CF _{T,EO} (°C)			
	Sample mass (mg)			
	0.100	0.500	1.000	5.000
1	0.7	0.6	0.6	0.5
5	0.5	0.4	0.4	0.3
10	0.4	0.3	0.3	0.2
20	0.2	0.1	0.0	-0.1
30	0.0	-0.1	-0.2	-0.3
40	-0.1	-0.3	-0.3	-0.5
50	-0.3	-0.4	-0.5	-0.7
100	-0.8	-1.1	-1.2	-1.6
150	-1.3	-1.7	-1.9	-2.4
200	-1.8	-2.2	-2.5	-3.2
250	-2.2	-2.7	-3.0	-3.9
300	-2.6	-3.2	-3.6	-4.6
400	-3.4	-4.2	-4.7	-6.0
500	-4.1	-5.1	-5.7	-7.3

Table III: Correction matrix for the determination of the correction factors for HPer DSC Diamond.

Sh (°C/min)	Correction factor for the peak temperature:			
	CF _{T,P} (°C)			
	Sample mass (mg)			
	0.1	0.5	1	5
1	0.6	0.5	0.4	0.1
5	0.5	0.3	0.2	-0.2
10	0.4	0.1	0.0	-0.5
20	0.1	-0.2	-0.4	-1.0
30	-0.2	-0.5	-0.8	-1.5
40	-0.4	-0.9	-1.1	-2.0
50	-0.7	-1.2	-1.5	-2.5
100	-1.9	-2.6	-3.1	-4.5
150	-3.0	-3.8	-4.4	-6.1
200	-4.0	-5.0	-5.5	-7.4
250	-5.0	-6.0	-6.6	-8.6
300	-6.0	-7.1	-7.7	-9.7
400	-8.0	-9.1	-9.7	-11.8
500	-10.0	-11.1	-11.7	-13.9

1.5. Symmetry check using liquid crystals

The ‘symmetry’ of the FSC’s furnace(s) with respect to heating- versus cooling performance has to be taken into consideration. When the furnace of a Fast-Scan Calorimeter is found to be ‘symmetrical’, it means that the correction factors found in the heating mode can be applied for correction in the cooling mode. Otherwise, a different correction matrix in cooling has to be built up.

For temperature calibration of FSC’s in both heating and cooling mode, secondary calibration standards can be used as reference materials. Sarge et al.ⁱⁱⁱ recommended substances for temperature calibration in the cooling mode. The secondary calibration standards used in the present report [3] are i.e. 4-cyano-4'-octyloxybiphenyl (M24), 4-(4-pentyl-cyclohexyl)-benzoicacid-4-propyl-phenyl ester (HP-53), 4'-ethyl-4-(4-propylcyclohexyl)-biphenyl (BCH-52) and cholesteryl oleyl carbonate (COC).

These substances (with exception of COC) are traceable standard reference materials from NIST (National Institute of Standard and Technology,

³ MettlerToledo sponsors the activities of the present study by supplying their temperature calibration set, which consists of the liquid crystalline secondary standards: M24, BCH-52, HP-53. The COC sample can be supplied by DSM Resolve

Gaithersburg, USA) and PTB (Physikalisch-Technische Bundesanstalt, Braunschweig, Germany).

The transition temperatures of these liquid crystals are:

- 55°C (crystalline-smectic), 67.1 °C (smectic-nematic) and 80.2 °C (nematic-isotropic) for M24;
- 73 °C, 93.6 °C and 120.5 °C (smectic-nematic) for HP-53;
- and 149 °C and 164.8 °C (smectic-nematic) for BCH-52. The smectic-nematic transition is recommended by the NIST to be used for DSC calibration;
- 20°C (smectic-cholesteric) and 40°C (cholesteric-isotropic); the transition temperatures of the liquid crystal COC.

Figure 5 presents the thermal transitions of HP-53 as a function of the heating (S_h) and cooling rate (S_c).

For the liquid crystals shown in Figure 6 one can conclude that the furnaces of the PerkinElmer HPer DSC Diamond used are fairly symmetrical, which means that the correction matrices of indium can be used also in the cooling mode.

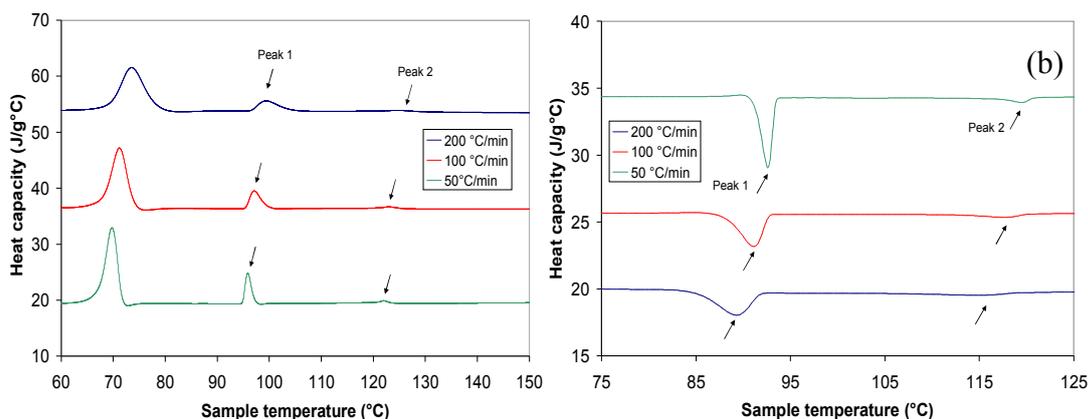


Figure 5: Determination of the transitions used for the symmetry check using HP-53 in (a) heating mode and (b) in cooling mode.

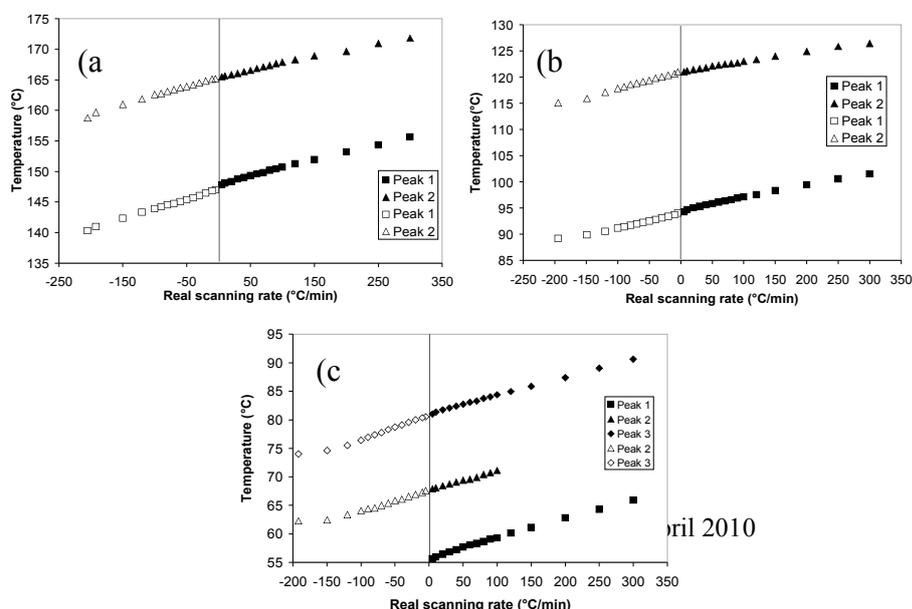


Figure 6: Check of the symmetry of HPer DSC Diamond using liquid crystals, (a) BCH-52, (b) HP53 and (c) M24.

2. Study of the cooling and heating performances and influence of purge gas

FSC's can be studied with respect to the influence of the purge gas on the cooling- and heating performances. Different purge gasses – helium, helium/neon⁴ and nitrogen – are used for this purpose (Figure 7). The red line is expected to shift in the direction of the arrow with better cooling performances.

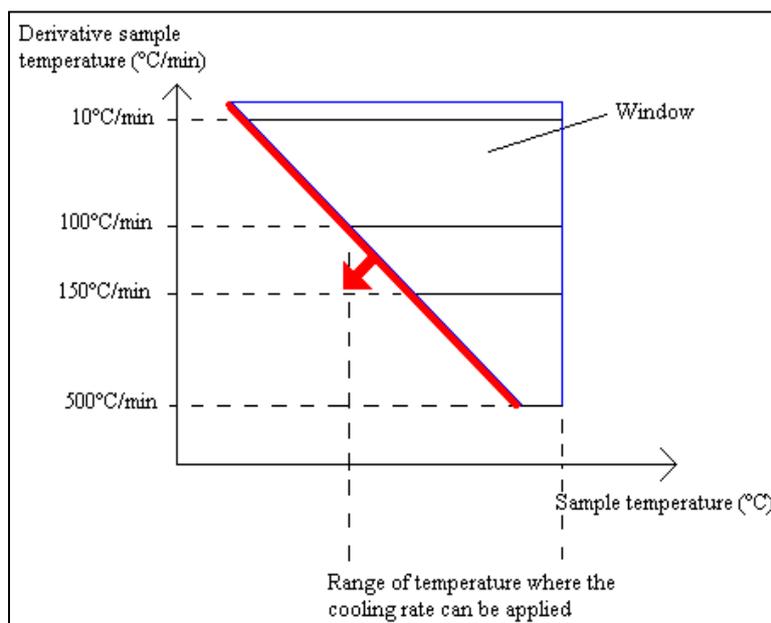


Figure 7: Sketch of the way to study of the cooling performance of HPer DSC.

As an example, see Figure 8, of cooling and heating performances, empty cell measurements of two types of PerkinElmer HPer DSC's have been done within the temperature range of -75 to 300 °C. Heating and cooling rates of 50, 100, 150, 200, 300, 400 and 500 °C/min have been applied. HeNe has been used as purge gas.

Concerning the heating performances, two factors must be considered. The first one is whether the heating rate programmed is actually reached and the second one is how fast the programmed heating rate is reached in reality.

⁴ With helium/neon or He/Ne is mentioned, throughout a mixture of 10% helium/90% neon is meant

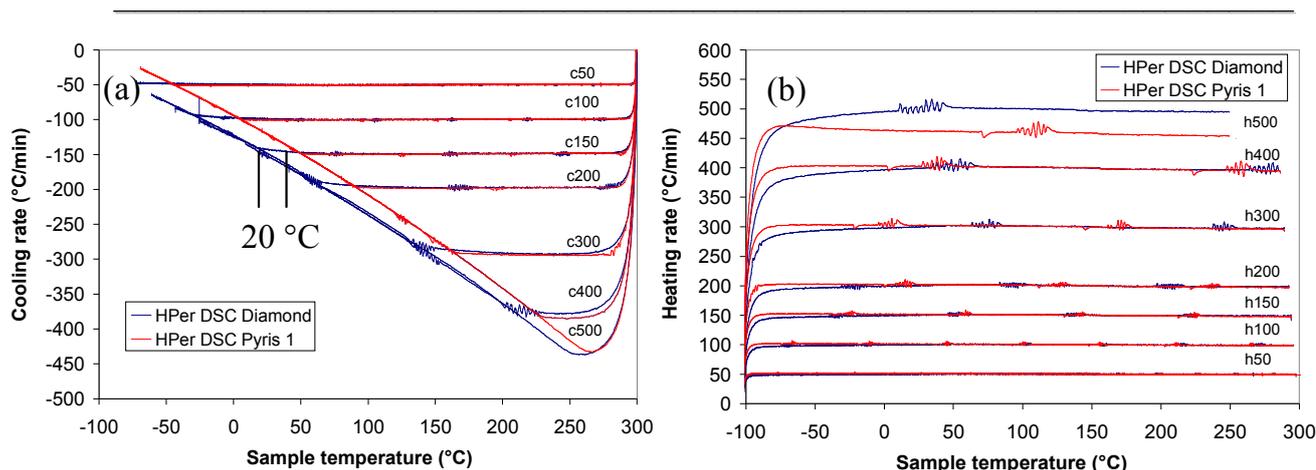


Figure 8: (a) Study of the cooling and (b) heating performances of HPer DSC.

The HPer DSC Pyris 1 used is equipped with a thermal analysis gas station (TAGS) in order to switch the type of purge gas, and thus HeNe, He and N₂ have been used to compare their influence on the cooling performance. Empty cell measurements were performed from -150 to 350 °C, using a cryofill liquid nitrogen cooling system, with applied heating and cooling rates varying from 5 to 500°C/min. Figure 9 presents the cooling performance of this type of FSC when using these various purge gasses. He turns out to be the purge gas with the best cooling performance, but of course it limits the maximum temperature of operation.

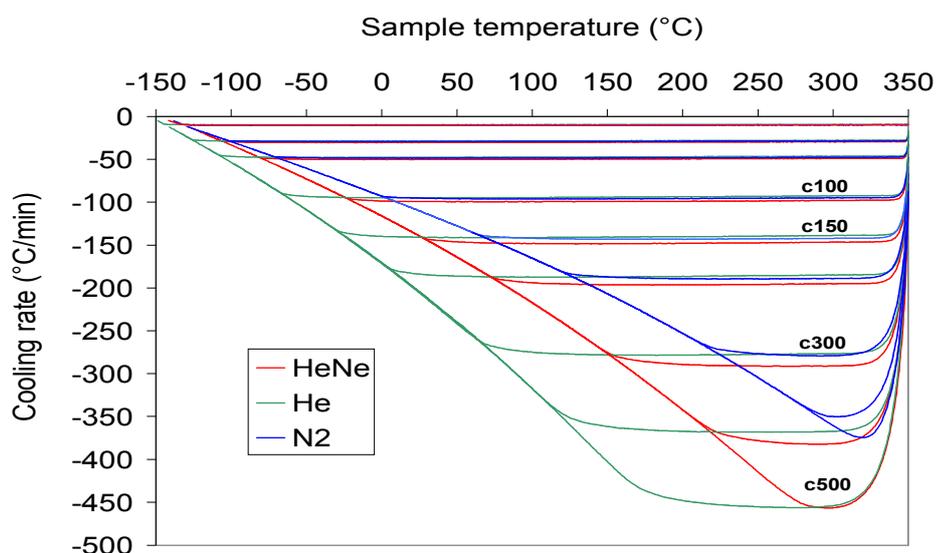


Figure 9: Study of the cooling performances of HPer DSC for various purge gasses.

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- ¹ An action within NaPolyNet: setting up research-intensive clusters across the EU on characterization of polymer nanostructure; EU-FP7-NaPolyNet / Coordination Support Action NMP-2007-2.1-3 / Characterisation of nanostructured materials; see <http://www.napolynet.eu>
- ¹ G. Vanden Poel and V.B.F. Mathot, *Thermochimica Acta* **446** (2006) 41
- ¹ S.M. Sarge, G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin, Temperature, heat and heat flow rate calibration of scanning calorimeters in the cooling mode, *Thermochim. Acta* **361** (2000) 1-20.



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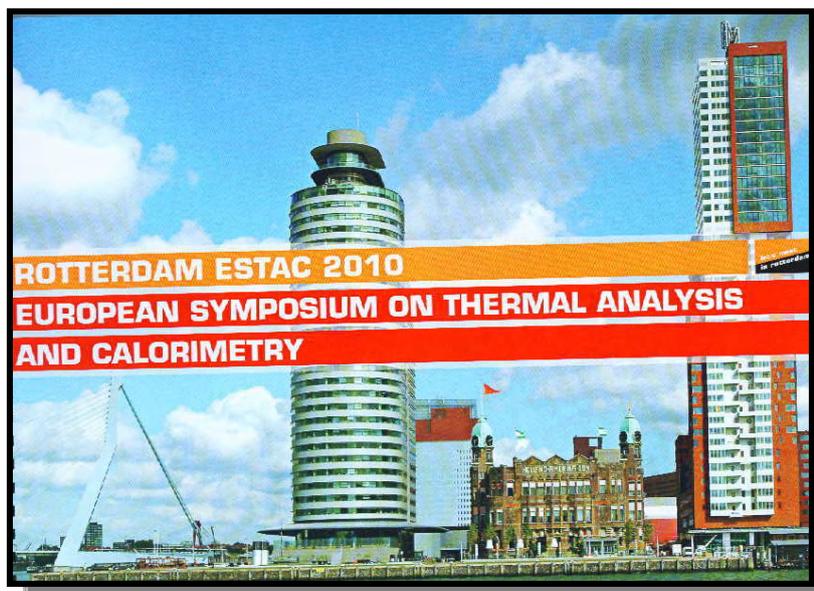
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High-Speed Furnace

Applications Newsletter 4/2009



Introduction

The estimated measuring time – along with the reliability and significance of the results – often plays an important role in almost any analytical question. The more intensively analysis methods are linked to production processes, the more important this becomes. While in the research and development of new materials, measuring times for the characterization of properties are scheduled as a matter of course, in in-process analysis, it is the capacity of production plants which determines the intervals at which product properties and product quality must be verified. Analyses for quality assurance must therefore often be realized on-line during the production process, or it must at least be possible to carry them out within the space of a few minutes for random sampling control.

In the past, it had been difficult to cover these areas by means of Thermal Analysis since conventional analyses take from 30 minutes to several hours, depending upon the measuring program. The measuring time depends primarily on the material to be tested and/or the temperature range which must be investigated for the characteristic material properties. Decisive parameters here are also the heating and cooling rates employed. These, in turn, are essentially dependent on the constructional design of the furnaces and analytical instruments. And that is where the newly developed high-speed furnace sets new standards.

With conventional thermoanalytical instruments, heating and cooling rates from 1 K/min to 20 K/min are common while the potential range is from 0.001 K/min to 100 K/min; the new high-speed furnace, on the other hand, allows for heating rates up to 1000 K/min. A heating rate of 500 K/min already reduces the measuring time from room temperature to 1000°C to under two minutes and thus increases the sample throughput tremendously.

Concept

The new high-speed furnace does not require a stand-alone instrument but extends the well-established 400 platform by another furnace type. The platform concept

allows for equipping a measuring instrument with a double-furnace hoisting device for two furnaces. The high-speed furnace can therefore be mounted on the double-hoisting device combined with other furnaces. Instead of a second furnace, an automatic sample changer (ASC) can optionally be used for the high-speed furnace. Modular flexibility and particularly the combinability of the high-speed furnace with the ASC saves a great amount of time and thus directly results in an increased sample throughput.

The following furnace types for the instrument series DSC 404 **F1**, DSC 404 **F3**, STA 449 **F1** and STA 449 **F3** are now available.

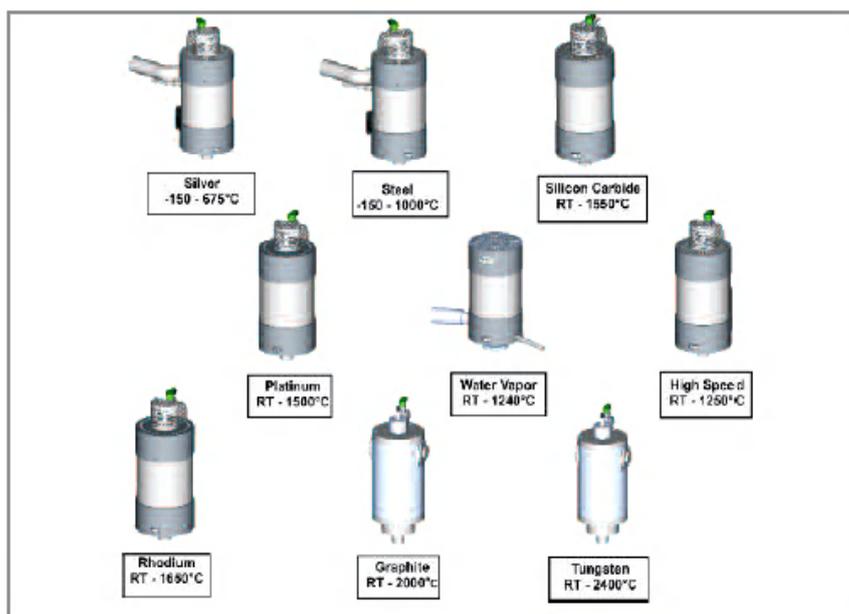


Fig 1: Different furnace types for the STA 449 and DSC 404

Setup

Figure 2 shows a cross section of the high-speed furnace. It can be seen that the high-speed furnace does not differ from the other furnaces of the 400 platform with regard to the main design points such as measuring heads, position of the sample temperature determination, gas flow, and separation of the sample and weighing chambers.

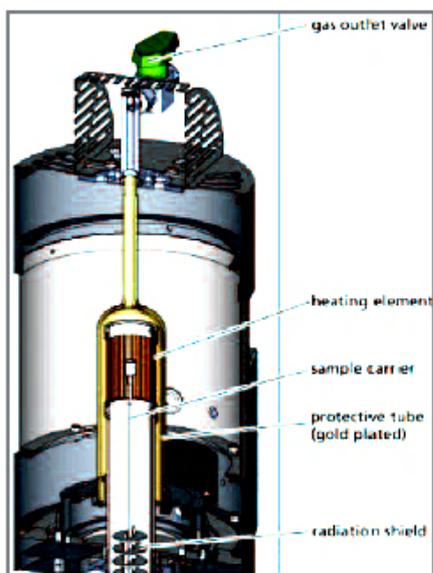


Fig. 2: Cross section of the high-speed furnace

The great variety of crucible types and materials can also be used in the high-speed furnace. This guarantees ideal comparability of the test results, even when obtained with different furnace types.

The actual heating element of the high-speed furnace consists of a resistance-heated platinum mesh. The protective tube separates the sample chamber from the exterior and renders it possible to work in pure sample atmospheres by means of evacuating and flooding of the sample chamber.

Test Results

In addition to the measurements at high heating rates, measurements at conventional heating rates of 10 K/min and 20 K/min were also carried out with the high-speed furnace in order to guarantee the comparability of test results with those obtained using other thermo-analytical instruments.

The presentation of the measured sample temperature versus time in Figure 3 shows linear heating rates in the range from 10 K/min to 500 K/min.

It was thereby confirmed that the high-speed furnace need not be limited to fast heating rates but that it is also perfectly capable of handling more conventional applications.

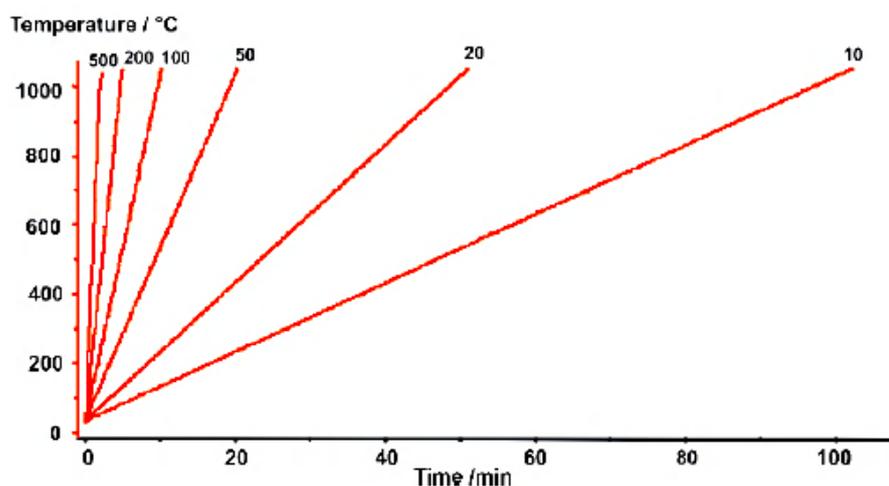


Fig. 3: Recording of the measured sample temperature versus time confirms linear heating rates of 10, 20, 50, 100, 200 and 500 K/min

Varying the heating rate under otherwise identical test conditions shifts the results to higher temperatures as the heating rate increases. This is a well-known correlation which further allows for the kinetic evaluation of the measured data by means of the specially developed NETZSCH *Thermokinetics*[®] software. If the correlation between the variation in the heating rates and the effects on the measured data is known and can be mathematically described, measurements can be carried out rapidly without having to forego the traceability of the measurement data to known sample properties, as are listed in the NETZSCH annuals, for example.

Using the pyrolysis of polypropylene (PP) as an example, the dependence of the results on the heating rate shall be pointed out.

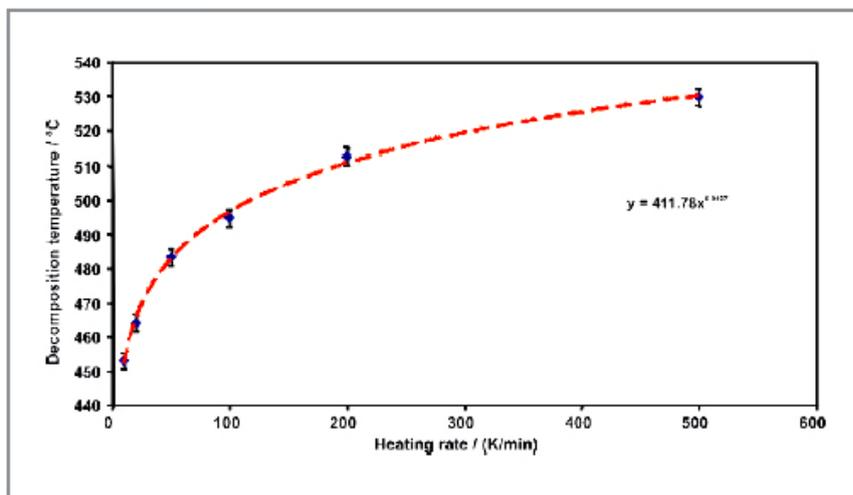


Fig. 5: Variation of the pyrolysis temperature of polypropylene for the heating rates 10, 20, 50, 100, 200 and 500 K/min

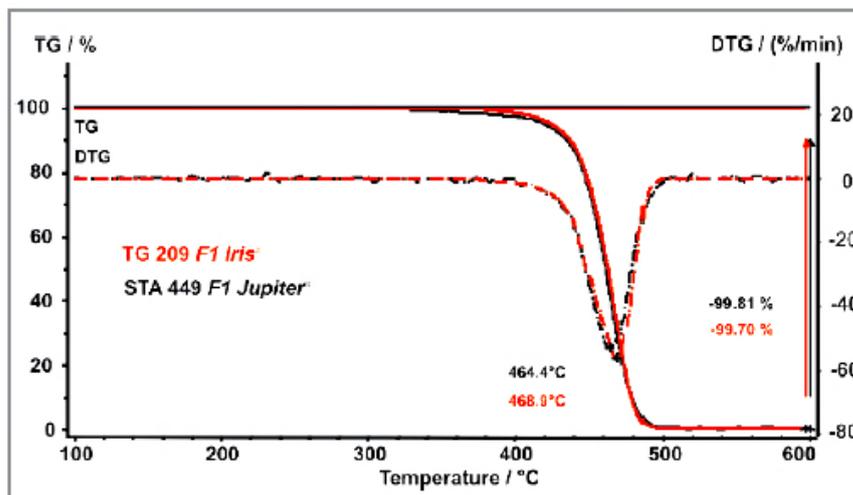


Fig. 4: Comparison of the measurement results of the pyrolysis of polypropylene (PP) with the TG 209 F1 Iris[®] (red) and STA 449 F1 Jupiter[®] (black)

Figure 4 initially shows that there are no significant differences in the measurement results when polypropylene is investigated under

identical conditions using two different thermogravimetric instruments (TG 209 F1 and STA 449 F1). This is noteworthy since the furnace geometry and therefore also the flow conditions of the purge gases are different.

In addition to the results of the relative mass change (TG), figure 4 shows its first derivative, i.e. the mass-change rates, as dashed lines (DTG). When evaluating the temperatures for the heating rates 10, 20, 50, 100, 200 and 500 K/min, where the mass-loss rate is at maximum (minimum of the DTG curve), the heating-rate dependence of the pyrolysis of propylene is obtained. This is presented in figure 5.

The logarithmic scaling of the heating rates yields a straight line, as can be seen in figure 6. The error bars shown in both figures 5 and 6 in the y-direction do not display real errors, but only depict a confidence interval of ± 2.5 K.

The thermal treatment of calcium carbonate (CaCO_3) results in a decomposition reaction above temperatures of 600°C where calcium oxide (CaO) and carbon dioxide (CO_2) are formed according to the following equation:

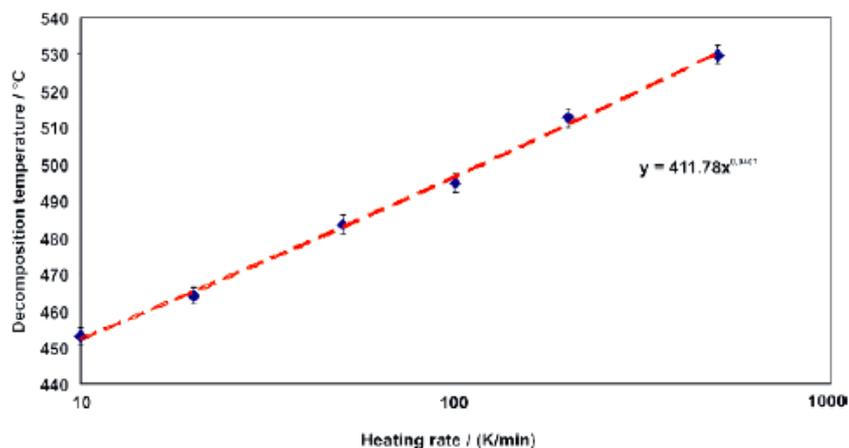
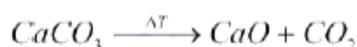


Fig. 6: Variation of the pyrolysis temperature of polypropylene for the heating rates 10, 20, 50, 100, 200 and 500 K/min

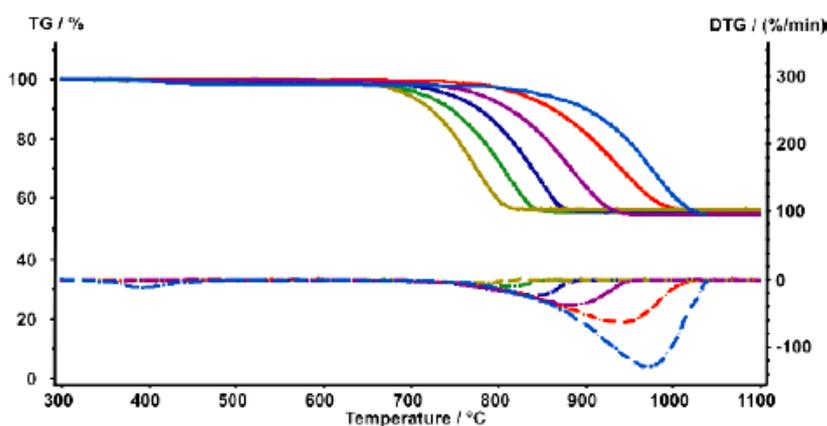


Fig. 7: TG-DTG results for CaCO_3 with varying heating rates from 10 K/min to 500 K/min

While the solid CaO remains in the sample crucible, the CO_2 and the purge gas flow are both leaving the instrument via the outlet. The amount of CO_2 accrued can be quantified as a mass loss.

Figure 7 presents the results of a test series which was carried out with the same measurement conditions as described for PP. The mass-loss steps are not dependent on the heating rate; the decomposition temperatures (DTG minimum) are shifted to higher temperatures as the heating rates increase.

The mass-loss rate increases from 5.1%/min to 128.8%/min when the heating rate is increased from 10 K/min to 500 K/min (Figure 9).

This shows that the influence of the heating rate on the measurement results follows a traceable law.

This relation is decisive for the comparison of measurement results which were determined at different heating rates.

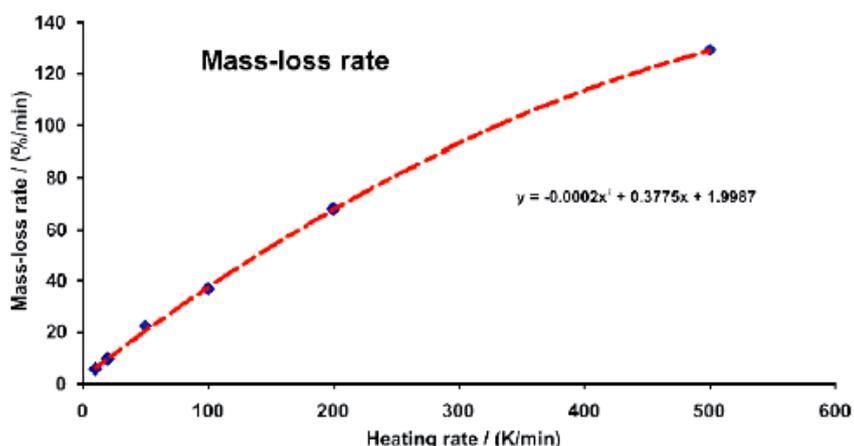


Fig. 9: Change of the mass-loss rate as a function of the heating rate

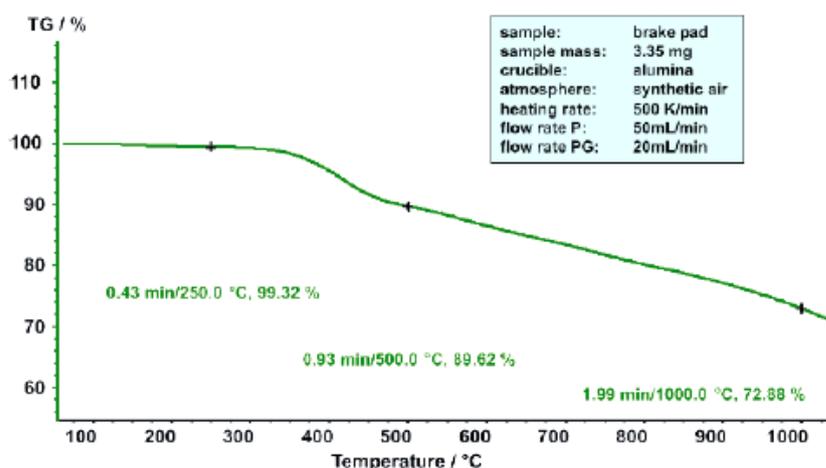


Fig. 10: Measurement result of a brake pad at a heating rate of 500 K/min

Materials for products such as brake pads can now be analyzed under operating conditions. During braking, kinetic energy is transferred into heat by means of friction. The material can thereby be exposed to very high temperatures within a very short time frame.

Heating rates of 500 K/min allow these extreme operating conditions to be analytically reproduced (figure 10).

Atmosphere:	inert, oxidizing
Sample carrier:	standard STA
Maximum heating rate (linear):	1000 K/min
Maximum sample temperature:	1250°C

Tab. 1: Technical data high-speed furnace

Summary

The new high-speed furnace constitutes an extension to the well-established 400 platform which enhances its already versatile potential. Some of this entails the possibility of combining the high-speed furnace with other furnaces on a double-hoist device or with an automatic sample changer (ASC). The comparability of the measurement results of the high-speed furnace with those of other thermogravimetric instruments was demonstrated using the pyrolysis of polypropylene as an example. This is an important prerequisite for the unrestricted utilization of the information content of measurements at heating rates of up to 500 K/min.

The dependence of the measurement results on the variation of the heating rate shows a linear correlation under logarithmic scaling of the heating rate. Therefore, comparisons with measurements at conventional heating rates are also possible. The mass-loss steps themselves are not dependent on the variation of the heating rates.

Also, using the thermal decomposition of CaCO_3 as an example, it was shown clearly that although the heating rate does have an influence on the measurement results, it also follows a very traceable law.

Using fast heating rates therefore does not result in any loss of information, and the fact that each measurement only takes a few minutes yields a tremendous gain in time which greatly increases the sample throughput and thus also the efficiency of the thermo-analytical instrumentation.

The thermogravimetric investigation of a brake pad at 500 K/min also allowed – in addition to the greatly increased throughput – for materials being exposed to extreme thermal conditions to be analyzed under operating conditions for the first time.

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Jaargang 32

