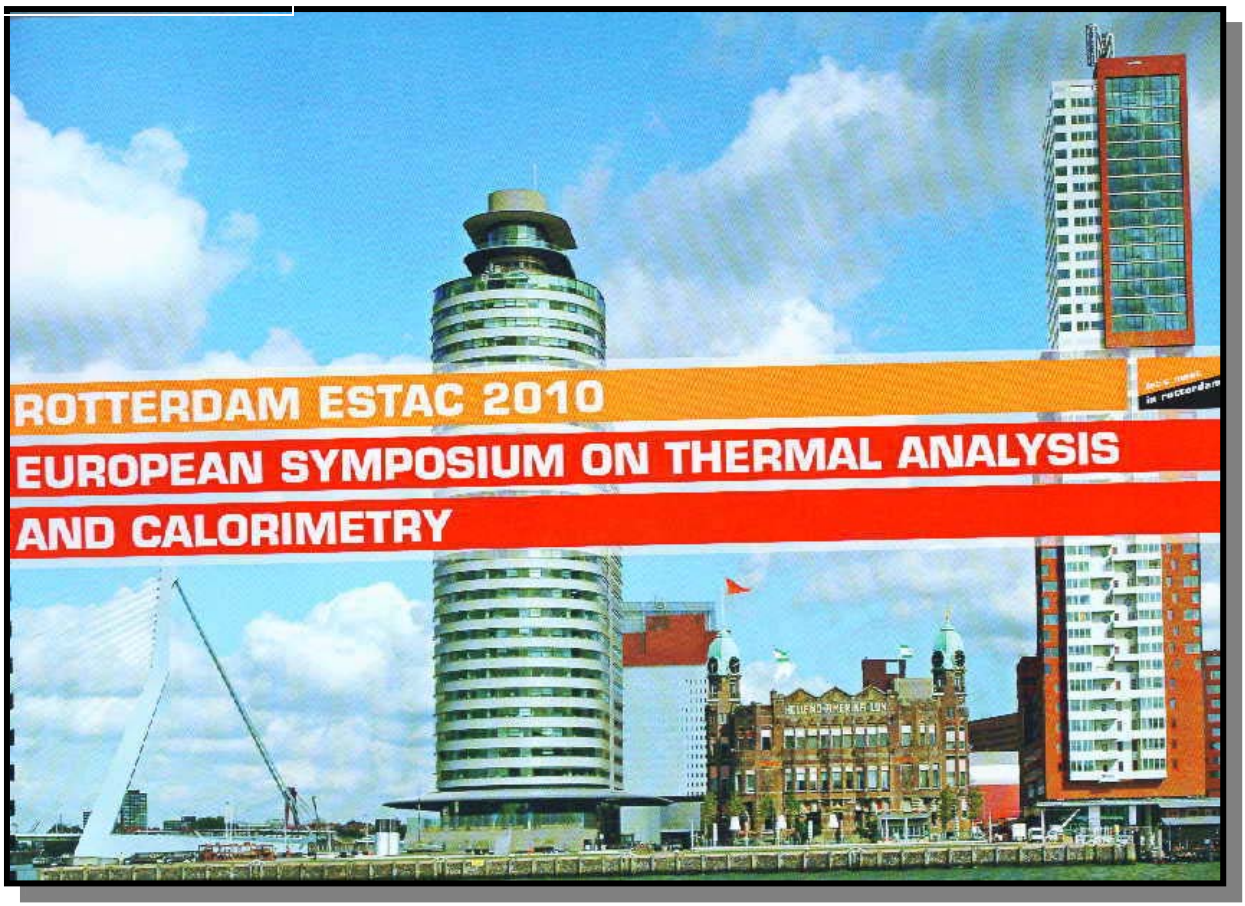
Thermische Analyse Bulletin

Het officiële orgaan van de Thermische Analyse Werkgroep Nederland nov. 2007

Conferentie data,
ESTAC 2010 , Programma TAD 2007,
persberichten, laatste instrumentatie nieuws, etc .


ROTTERDAM ESTAC 2010
EUROPEAN SYMPOSIUM ON THERMAL ANALYSIS
AND CALORIMETRY

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.**

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REDACTIONEEL

Helaas heeft de planning gedurende mijn verhuizing niet gewerkt. Niet alle bijdragen op tijd binnen en dan ook nog weken zonder telefoon en internet.
Er zijn deze keer behoorlijk veel bijdragen en advertenties. Hiervoor een woord van dank aan alle firma's (TA instruments, Netzsch, Mettler Toledo) die hier hun steentje hebben bijgedragen. Alle inzendingen zijn gehonoreerd.
De aankondiging van de TAD 2007 met het programma met veel interessante bijdragen is rechtstreeks geschied. We hopen op veel deelnemers, die zich de kans niet laten ontnemen om tevens het NLR te bezoeken.

Inhoudsopgave

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
The Netherlands
tel. : + 31 15 284 3580
fax : + 31 15 284 3958
e-mail : wim.deklerk@ tno.nl

TAD 2007

Dit jaar zal de TAD worden gesponsord door het nationale Lucht- en ruimtevaart laboratorium.

Noordoostpolder

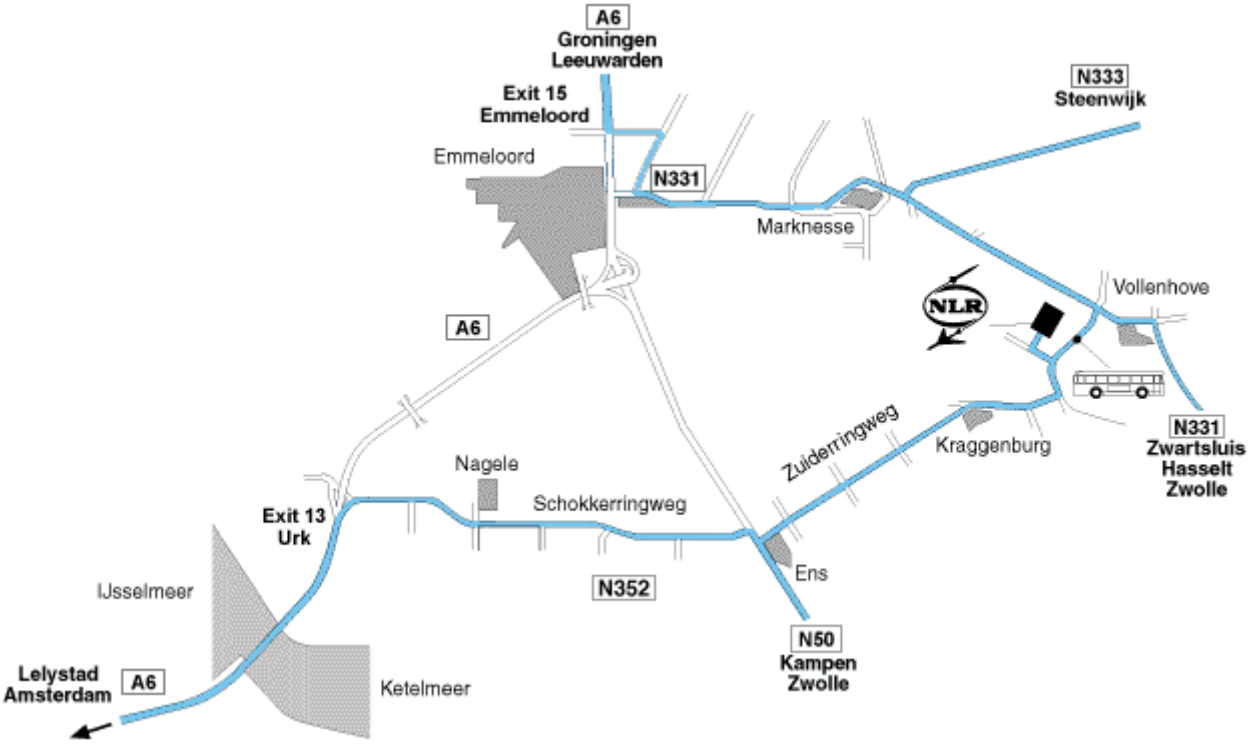
NLR Noordoostpolder ligt bij Marknesse in de Noordoostpolder.

Bezoekadres:

NLR Noordoostpolder
Voorsterweg 31,
8316 PR Marknesse
Tel. (+31) 527 248444

NLR Noordoostpolder met het openbaar vervoer:

Vanaf Amsterdam, Schiphol, Utrecht, etc.:
Vanuit de meeste richtingen, is NS station Zwolle het beste uitgangspunt. Neem vanaf daar bus 71 richting Emmeloord. Uitstappen bij halte 'Waterloopkundig Laboratorium' bij Vollenhove. Vanaf daar is het 10 minuten lopen.



TAWN

THERMISCHE ANALYSE WERKGROEP NEDERLAND

<u>Programma TAD-2007</u>
Locatie : Nationaal Lucht- en Ruimtevaartlaboratorium,
Marknesse (NLD)
Datum : 30 november 2007
(Routebeschrijving: zie volgende pagina)

09.30 uur **Ontvangst met koffie**

10.00 uur **Opening door dr. P.J. van Ekeren, voorzitter TAWN**

10.05 uur **<u>Ir H.G.S.J. Thuis,</u>** ***"Introductie van het Nationaal Lucht- en Ruimtevaartlaboratorium"***

10.25 uur **<u>Karel van der Sijde (NLR)</u>**, ***"Thermische Analyse bij NLR"***

10.45 uur **Koffie / Thee**

11.15 uur **<u>Nico Gotzen (Vrije Universiteit Brussel, B)</u>** ***"Local thermal analysis of polymers using heated AFM probes: micro- and nano-thermal analysis"***

11.40 uur **<u>Peter van Puyvelde (KU – Leuven)</u>** ***"Rheo DSC, a novel hybrid technique***

for the simultaneous measurement of calorimetric and rheological properties"

12.00 uur **An Hardy (Limburgs Universitair Centrum, B)**, ***"Understanding the formation of (ultra) thin oxide films by aqueous CSD: The importance of hyphenated thermal analysis"***

12.25 uur **Lunch**

13.35 uur **TAWN ledenvergadering 2007**

14.30 uur **Wim de Klerk (TNO Defensie en Veiligheid, NLD)** ***"Lifetime study on gas generating composition"***

14.50 uur **Thijs Pijpers[1,2]-Vincent Mathot[1,2] ([1] SciTe, [2] Katholieke Univ. Leuven)**
Optimization of instrument response and resolution of standard- and high-speed power compensation DSC and applications

15.10 uur **Koffie / Thee**

15.35 uur **Rondleiding op het laboratorium van het NLR**

16.30 uur **Afsluiting TAD-2007**

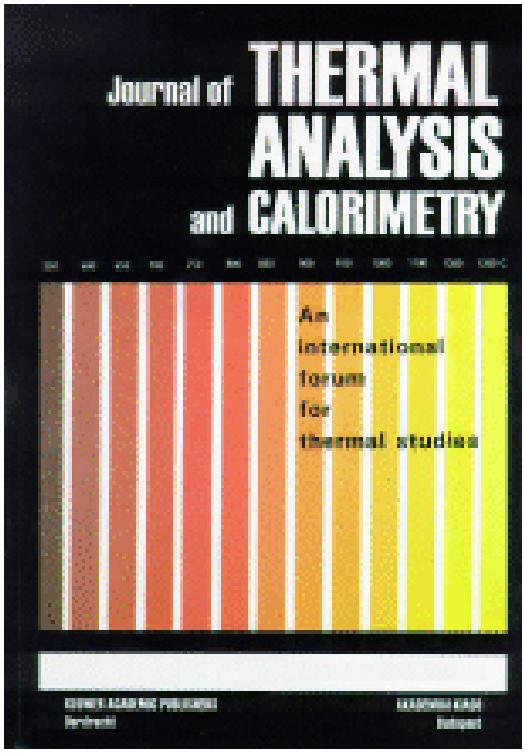
Agenda ledenvergadering van TAWN - 2007

1. ***Opening door de voorzitter***
2. ***Verslag van vorige ledenvergadering (November-2006)***
3. ***Jaarverslag van de voorzitter***
4. ***Financieel jaaroverzicht 2006 / Benoeming nieuwe leden kascommissie***
5. ***Internationale contacten en bijeenkomsten (o.a samen met de GEFTA, ESTAC, NATAS)***
6. ***TA-bulletin en website van TAWN***
7. ***Thermische Analyse Prijzen***
8. ***Samenstelling bestuur***
   De heren G. VandenMooter en W. de Klerk zijn aftredend en stellen zich beide herkiesbaar.
9. ***Rondvraag***
10. ***Sluiting***

Hotel information in the vicinity of NLR (Noordoostpolder)

Hotel Zwartewater **De Vlakte 18** **8064 PC ZWARTSLUIS** **Tel. (0)38 38 66 444** **Fax. (0)38 38 66 275** **www.hotel-zwartewater.nl**	**20 min. from NLR by car**
Hotel Restaurant "de Herberg" **Kerkstraat 1** **8325 BH VOLLENHOVE** **Tel. (0)527 24 34 66**	**7 min. from NLR by car**
Van Saaze **Dam 16** **KRAGGENBURG** **Tel. (0)527 252 353** **Fax (0)527 252 559** **http://www.hotelvansaaze.nl/** **(16 rooms)**	**7 min from NLR by car**
Hotel van der Valk **Het Hooiveld 9** **8302 AE EMMELOORD** **Tel. (0)527 612 345** **Fax (0)527 612 845** **www.valk.nl**	**20 min from NLR by car**

Vaker publiceren in de thermische analyse tijdschriften nu de Impact Factor is verhoogd!



Onderzoeksresultaten worden over het algemeen gepubliceerd in de wetenschappelijke tijdschriften. De twee bekendste tijdschriften op het gebied van de thermische analyse en de calorimetrie zijn het "Journal of Thermal Analysis and Calorimetry" (JTAC), uitgegeven door Springer, en "Thermochimica Acta" (TA), uitgegeven door Elsevier. De web-adressen van deze tijdschriften zijn respectievelijk www.springer.com/journal/10973 en http://www.elsevier.com/wps/find/journaldescription.cws_home/500855.

Helaas wordt veel zeer interessant werk op het gebied van de thermische analyse vaak niet gepubliceerd in één van deze tijdschriften. Daar kunnen verschillende redenen voor worden aangedragen, waarvan er één de zogenaamde Impact Factor is.

De Impact Factor van een tijdschrift geeft aan hoe vaak een artikel in dat tijdschrift gemiddeld wordt geciteerd. De Impact Factor van tijdschriften wordt bepaald door het Institute for Scientific Information (ISI). Jaarlijks worden Journal Citation Reports (JCR) opgesteld waarin wetenschappelijke tijdschriften worden geëvalueerd en vergeleken.

De wijze waarop de Impact Factor wordt berekend wordt verduidelijkt aan de hand van de Impact Factor van het JTAC in het jaar 2006. In alle tijdschriften die door het ISI worden geëvalueerd telt men dan het aantal referenties naar artikels die in de twee voorgaande jaargangen van JTAC zijn gepubliceerd (dus in 2005 en 2004). Ook telt men het totale aantal artikels dat in

2005 en 2004 in JTAC is gepubliceerd. De Impact Factor verkrijgt men door deze twee getallen op elkaar te delen. In 2006 waren er 520 citaties naar artikels gepubliceerd in 2005 en 705 citaties naar artikelen gepubliceerd in 2004: in totaal dus 1225 citaties. In totaal stonden er in 2005 459 artikels in JTAC en in 2004 393 artikels, in totaal in deze twee jaren dus 852 artikels. De Impact Factor is dan 1225 / 852 = 1,438.

De Impact Factor in van belang omdat deze tegenwoordig mede wordt gebruikt om een kwaliteitsoordeel uit te spreken over onderzoekers en onderzoeksgroepen. Onderzoekers willen dus graag publiceren in een tijdschrift met een hoge Impact Factor. Helaas was de Impact Factor van de thermische tijdschriften een aantal jaren geleden door verschillende oorzaken nogal laag. Bijvoorbeeld in 1998 was de Impact Factor van JTAC 0,655 en die van TCA 0,769.

Rondom de eeuwwisseling is de redactie van JTAC extra aandacht gaan schenken aan de Impact Factor. Gelukkig hebben de maatregelen effect gehad: gestaag steeg de Impact Factor en vanaf 2004 is deze redelijk constant op ruim 1,4. Ook de redactie van TCA is succesvol geweest van in 2006 bereikte ook dit tijdschrift een Impact Factor van 1.417.

Zowel JTAC als TCA zijn nu dus aantrekkelijker geworden voor het publiceren van onderzoeksresultaten! Natuurlijk kan de Impact Factor nog verder stijgen. In ieder geval heeft de redactie van JTAC daar nog wel wat ideeën over en ik ben ervan overtuigd dat ook de redactie van TCA niet stilzit. Maar ook is het daarvoor van belang dat wij allen als belangstellenden in de thermische analyse ons betere werk publiceren in de thermische analyse tijdschriften! Ik ben ervan overtuigd dat dit op termijn ook het aanzien van ons vakgebied ten goede zal komen.

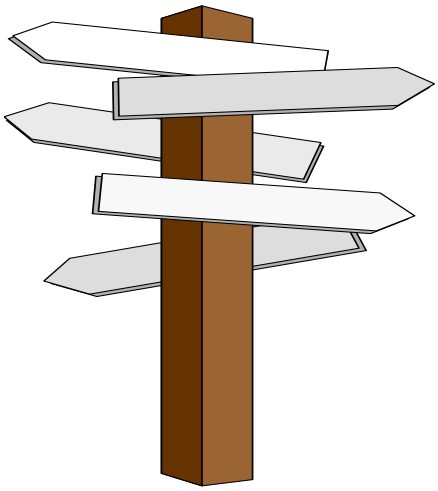
Manuscripten die u gepubliceerd wilt zien in JTAC kunt u aanbieden bij mij als regionaal redacteur van JTAC (e-mail adres: Paul.vanEkeren@tno.nl). Een manuscript dat u wilt publiceren in TCA kunt u sturen naar Christoph Schick (e-mail adres: christoph.schick@physik.uni-rostock.de.

Ik hoop de komende tijd meer publicaties van Nederlandse en Belgische collega's te zien in JTAC en TCA.

Paul van Ekeren,
regionaal redacteur van JTAC.

N.B. Dit artikel is geschreven op persoonlijke titel en geeft niet noodzakelijkerwijs de mening van het bestuur van de TAWN weer.

CONGRESSEN, SYMPOSIA, CURSUSSEN,



Thermal Analysis and Calorimetry 2008

1-2 April, 2008
Teddington, UK
Sam Gnaniah
Tel: +44 (0)208 943 6174
email: tac2008@npl.co.uk
For more information click www.npl.co.uk/tac2008

14 International Congress on Thermal Analysis and Calorimetry

14 - 18 September, 2008

São Pedro, Brazil

Secretary
Luci D. B. Machado
secretary@ictac14.com.br

Chairman
Valter J. Fernandes Jr.
chairman@ictac14.com.br

For more information view the following pdf documents.

International Congress Announcement And First Call For Papers (2008 ICTAC) - low

Volgende Pagina's bevatten bijdragen van TA firma's.
(buiten de verantwoordelijkheid van de redactie).

Job: FIELD SERVICE ENGINEER BNL

TA Instruments – a Division of Waters (WAT: NYTE)

TA Instruments, the market leader in Thermal Analysis and Rheology is known for his technology innovations and excellent customer support. We are a very dynamic team, with excellent financial performances. Because of our steady growth and recent acquisitions we are looking to expand our BNL team.

Major Responsibilities

Installs, basic operation training, services and maintains currently produced thermal analysis and rheology instruments; handles general customer interface problems. Promoting and selling support products.

Essential Duties And Responsibilities include the following. Other duties may be assigned.

- **Provides customer support; training, diagnoses and troubleshoots customer problems and distinguishes between technical problems, training and/or application issues. Refers to the appropriate resource in order to resolve outstanding issues.**
- **Economic use of replacement parts and managing the returns process. Responsible for managing car stock and maintaining their tools so they are clean, functioning, where required calibrated and in good order.**
- **Repairs, installs, and uses all currently supported instrument models and accessories; calibrates instruments for optimal performance.**
- **Provides information to customers regarding service products and offerings; effectively sells service products and contracts.**
- **Should gain extensive knowledge of applications software; provides startup training in the operation and application of either thermal and/or rheology instruments to the customer during or after the installation.**

- **Responsible for preparing and timely submission of a variety of reports, logs and documentation of service and repair activities. This includes service reports, product reliability report;.tracking reports (work in progress and completed work)**
- **Responsible for maintaining up-to-date manuals, service notes, drawings, and other materials needed for effectiveness**
- **Is adept and dependable in utilizing the companies' service CRM solution up to the required level and within the essential time frames.**
- **Ensure compliance with local safety standards**
- **Establishes and maintains prompt professional communications with customers and internal resources. Actively engage in exchange of information between sales and support.**

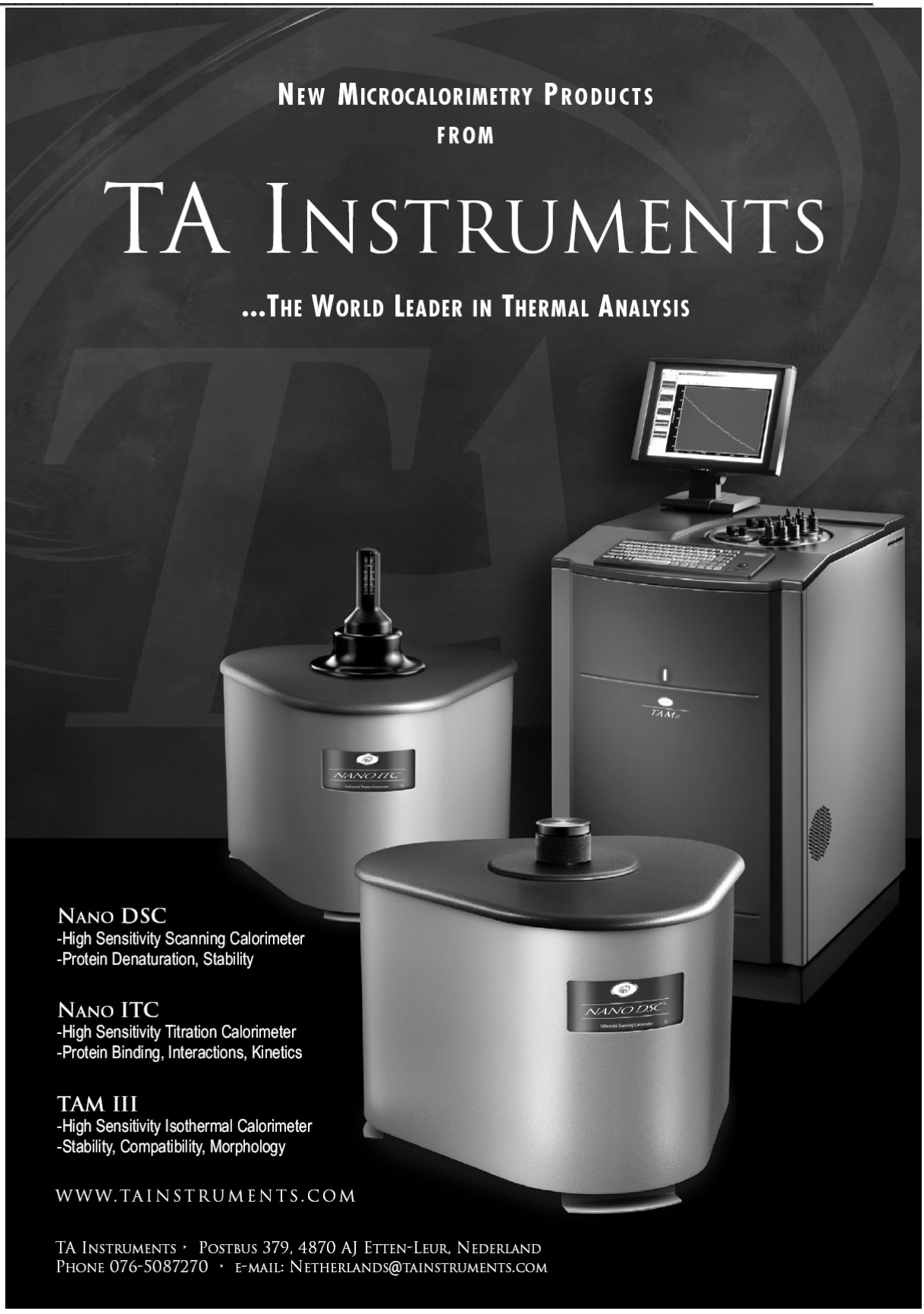
Qualification Requirements

To perform this job successfully, an individual must be able to perform each essential duty satisfactorily. The requirements listed below are representative of the knowledge, skill, and/or ability required. Reasonable accommodations may be made to enable individuals with disabilities to perform the essential functions.

Education And/Or Experience

Education: All levels

Knowledge normally acquired through completion of a two (2) year degree in electronics, science , instrumentation or other closely related field or equivalent combination of education and experience. Prior field service experience is highly desirable.



Advertentie TA

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Ankersmid

The Series VTGA Analyzers provide thermogravimetric testing capabilities with High-Temperature ranges up to 1000ºC and High-Pressure ranges up to 150 bars.

"With VTI's unique VTGA Systems, the pressure's really on!"

VTI?s Model VTGA ThermoGravimetric Analyzers are designed for thermal reaction studies using steam, organic vapors, hydrogen, methane, carbon dioxide and other gases, including corrosive gases.

Using the continuous flow method, the VTGA Analyzers provide isotherms, isobars and time course data for the study of?

- **General gas/solid reactions**
- **Oxidation/reduction of metals**
- **Degradation of ceramics**
- **Catalysts, zeolites, activated carbons and other specialty materials**
- **CO_2 Sequestration techniques**

?all at pressure ranges up to 150 bars and temperature ranges up to 1000°C.

Instrument without front panel in place to show internal subsystem details

Specifications?

- **The Model VTGA-50 has standard pressure/temperature range of 50bars to 800°C with option to 1000°C ?and the VTGA-150 has standard range of 150bars to 400°C with option to 750°C**

- **Heating rates adjustable from a minimum of 1°C/min to a maximum of 20°C/min**
- **Microbalances with sensitivities down to 0.1 µg and capacities up to 25 grams**
- **Optional magnetic suspension microbalances available for handling corrosive testing environments**
- **Standard instruments handle helium plus three reaction gas inputs, with additional gas ports available as options**
- **Optional steam generating capability**
- **Can be easily integrated with customer-supplied mass spectrometer**
- **VTGA Analyzers are complete instruments including computer and software package**
- **User-friendly Lab Windows/CVI software**
- **Comprehensive Data Analysis Package using Microsoft Excel**

For more technical details for the VTGA Analyzers,
please contact Ankersmid BV at: +31 – (0)-162-408910

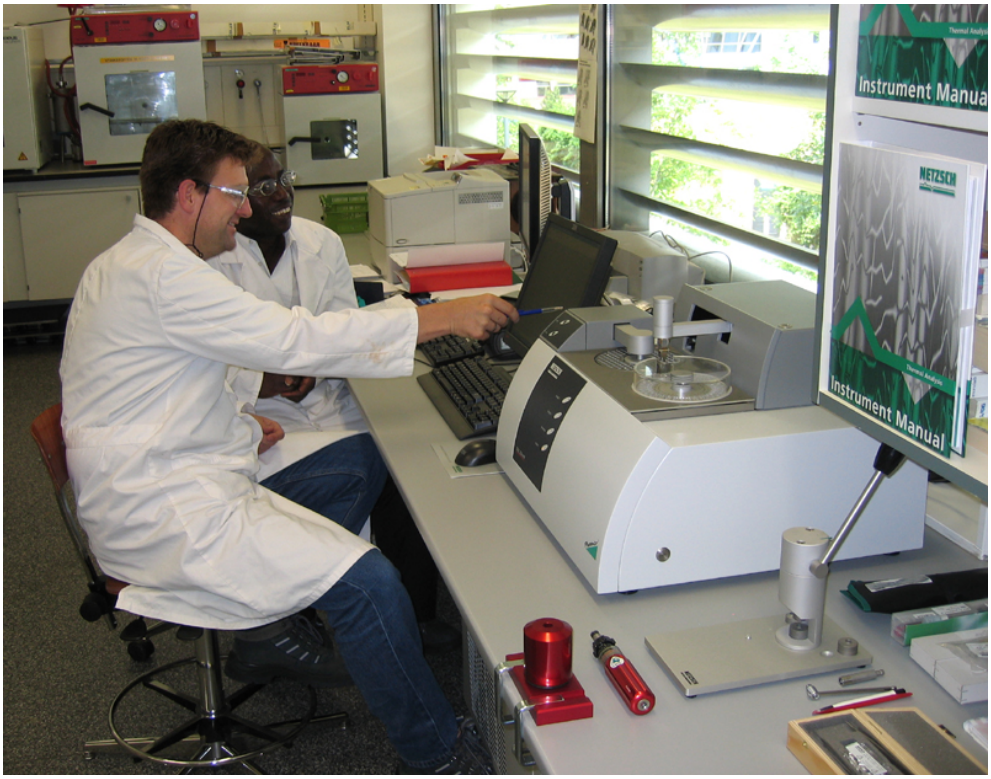
ORGANON in Oss kiest de Netzsch DSC 204 *F1 Phoenix* voor farmaceutisch onderzoek.

Na een intensieve proefperiode van 4 DSC's van verschillende merken kwam de Netzsch *F1* als winnaar naar voren

NV Organon is een business unit van Akzo Nobel en is het grootste internationale Nederlandse biofarmaceutische bedrijf. Het bedrijf heeft momenteel ongeveer 14.000 medewerkers verspreid over meer dan 50 landen in dienst. Hiervan zijn er zo'n 5000 mensen werkzaam in Nederland, verspreid over verschillende locaties. Organon ontwikkelt, produceert en verkoopt geneesmiddelen, waarbij gynaecologie een belangrijke plek inneemt. Bij Organon ligt een groot accent op medisch en farmaceutisch onderzoek, om zo te streven naar een nog veiliger en gezondere toekomst voor volgende generaties.

Veiligheid staat voorop bij de productie van medicijnen. Binnen de afdeling Proces chemie worden in het Kilolab de nieuwe farmaceutische verbindingen voor de eerste maal op kilogram-schaal geproduceerd. Hierbij is veiligheidsonderzoek van groot belang. Voor het onderzoek van de thermische stabiliteit gebruikt Organon onder andere een Calorimeter. Dit systeem kan slechts één meting per dag uitvoeren aan relatief grote (en dus kostbare) monsters. Een DSC werkt met kleinere samples en kortere meettijden waardoor de efficiency sterk kan worden verbeterd. Organon nodigde de 4 bekendste thermische analyse leveranciers, waaronder Technex/Netzsch uit, om het nieuwste model DSC een paar weken op proef te leveren. Olaf Post, onderzoeker in het Kilolab vertelt hierover:" Gedurende de proefperiode is de apparatuur onder praktijkomstandigen uitvoerig aan de tand gevoeld. Op deze manier hebben we een uitstekende indruk gekregen van de robuustheid, betrouwbaarheid en het bedieningsgemak. De Netzsch DSC 204 F1 Phoenix kwam als winnaar uit de bus. De degelijke constructie en de probleemloze bediening van de DSC en AutoSampler, in combinatie met de lokale support, de nuttige accessoires en Advanced Software waren voor ons doorslaggevend."

Loran Mak, accountmanager bij Technex voegt hieraan toe: "Ik waardeer het bijzonder dat Organon met open vizier kennis wilde nemen van alle relevante sterke en zwakke punten van de DSC apparatuur van de 4 grootste fabrikanten. We zien dat de nieuwe Netzsch *F1* en *F3* series zeer goed worden ontvangen door de markt. Mede hierdoor is de omzet van de Netzsch thermische analyse apparatuur in Europa in de periode van 2004 tot 2007 meer dan verdubbeld en is Netzsch wereldwijd de op-één-na grootste producent van thermische analyse apparatuur geworden.


Instrument Manual
NETZSCH
Instrument Manual


NETZSCH
Instrument Manual

Advertentie Technex

Review of European DEA Seminar for Cure Monitoring in Frankfurt

How can one tell whether the curing process for a paint, adhesive or polymer resin has finished? Or how far along curing has progressed, or how high the degree of curing is? Dielectric Analysis (DEA) can answer questions like these – not only in routine laboratory work, but also in situ.

NETZSCH-Gerätebau GmbH held its first European DEA seminar on June 26th - 27th, 2007. We had the pleasure of welcoming a total of 15 participants from Switzerland, the Netherlands, France, Denmark, Austria and Germany at this seminar in Frankfurt. Both long-time DEA specialists and newcomers in the field of cure monitoring took part in this event.

The first day focused on describing the DEA technique and its most varied applications. Following an introduction to the field of Thermal Analysis and especially to Dielectric Analysis by Dr. Gabriele Kaiser, Head of the Education and Training Department at NETZSCH-Gerätebau GmbH in Selb, the employment of DEA as an in situ measuring method for conductive thermoplastics was presented by Dr. Dirk Lellinger of DKI in Darmstadt. Stephan Knappe, Head of the Department for Sales & Applications Support at NETZSCH-Gerätebau GmbH, reported in detail about the DEA instrument technique, focusing especially on the new features of DEA sensors and accessories. After lunch, Jürgen Zöller of the NETZSCH Sales Department introduced the latest product developments at NETZSCH Analyzing & Testing. Dr. Harald Preu of Infineon Technologies in Regensburg gave a lecture using

measuring examples to illustrate the successful use of DEA in the manufacturing of supra-conductors. Martin Rosentritt from the University of Regensburg presented the different influences involved in the UV-curing of dental masses. Practical applications in the paints and adhesives sector were presented by Stephan Knappe, whereby particularly high interest was shown in the thermokinetic analysis of DEA measuring data for calculation of the degree of curing.

The following day, correlations between the DEA technique and other thermoanalytical measuring methods such as DSC and DMA were illustrated by Dr. Gabriele Kaiser. Michael Grüner, also of the NETZSCH Sales Department, presented the various DEA sensor types for different applications. With that, the practical part of our session had begun. At two DEA working stations, handling and software were demonstrated, measurements on epoxy resin systems were carried out, and measurement results were discussed. Great emphasis was thereby placed on the different influencing factors such as sensor choice, sample coating thickness, sample preparation, measuring parameters and curve interpretation. Afterwards, Martin Kränzler from Automotive Lighting in Reutlingen lectured about his experiences using inline cure monitoring for a continuous paint process.

During the final discussion, a proposition was raised to have an annual users' meeting for sharing experiences; this met with the interest of all participants. The next DEA seminar in 2008 will therefore also be combined with a users' meeting.

For more information, see www.thermischeanalyse.nl or www.netzsch-thermal-analysis.com

Technex introduceert de nieuwe e2k Calorimeter van Cal2k

CAL2k is een innovatief Zuidafrikaans bedrijf met meer dan 30 jaar ervaring in het ontwikkelen en produceren van geavanceerde calorimeters. De Cal2k systemen zijn speciaal ontworpen met het oog op maximale nauwkeurigheid en betrouwbaarheid tegen een competatieve prijs.

Alle Cal2k calorimeters zijn Oxygen Bomb Calorimeters die werken volgens de ISO 1928, DIN 51900 en ASTM D240. Veel conventionele Calorimeters werken

nog met een watermantel en vergen vóór iedere sample meting een aparte kalibratie meting, waardoor er minder minder efficiënt wordt gewerkt. De geavancerde Cal2k systemen zijn daarentegen volledig droog en bieden de hoogste graad van automatisering in zowel de kalibratieprocedure als de testprocedure. Hierdoor is de nauwkeurigheid optimaal en zijn de testtijden extreem kort. De kalibratiecurves worden opgeslagen in het geheugen van het reactievat, waardoor vergissingen onmogelijk zijn. De 8 temperatuursensoren

werken met een resolutie van 0,000001°C en maken een reproduceerbaarheid van beter dan 0,1% mogelijk.

Na het research-model, de Cal2k-1, en het economy-model de Cal2k-ECO, introduceert Technex de nieuwe e2k. De e2k combineert de snelheid en nauwkeurigheid van het research-model met het bedieningsgemak van het economy-model. Terwijl de meting loopt in het eerste reactievat, kan het 2^{e} reactievat worden geprepareerd. Op deze manier kunnen 10 metingen per uur worden uitgevoerd.

De Cal2k systemen worden onder andere toegepast voor vaste en vloeibare brandstoffen, in de voedingsmiddelen industrie, diervoeding, cement industrie, baksteen productie, munitie en explosieven productie en pyrotechniek.

TOPEM®: Measurement of Phase Transitions of Metastable Systems
Melting and Crystallization of Polymers and Organic Solutions

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ABSTRACT

The total heat flow measured by DSC can be separated in a sensible and in a latent heat flow. TOPEM® is the technique which allows to measure both directly and independently if adequate conditions are met. The reversing and non-reversing heat flow measured by conventional temperature modulated DSC cannot be assigned to the sensible and the latent heat flow.

Metastable systems can exist in a state close to equilibrium or far away from it. It will be shown, that the latent heat flow of a system depends on the metastable state or on the actual deviation from equilibrium. For example the latent heat flow of a process in equilibrium is zero.

The conditions required for analyzing melting processes using TOPEM® are discussed. If these conditions are fulfilled, the reversing heat flow measures processes that occur under equilibrium conditions and the non-reversing heat flow processes that involve supercooling or superheating. This distinction allows melting processes to be classified and crystal structures of differing stability to be differentiated. The latent heat flow therefore is a measure of the stability of a thermodynamic system. This will be shown and discussed using the melting and crystallization process of polymers and metastable solutions of organic materials.

INTRODUCTION

The measurement and interpretation of melting processes using temperature modulated DSC (TMDSC) is one of the more demanding tasks in thermal analysis. This is possibly the reason why a number of ideas and proposals can be found in the scientific literature that do not stand up to a critical analysis. Despite this, TMDSC can provide interesting and important information about melting behavior that would otherwise be difficult to obtain. Starting out from the basic principles of melting behavior discussed in reference [1], we want to show with the aid of suitable examples how melting behavior can be investigated using TOPEM®.

Basic principles of temperature modulated DSC.
Measurement principles and requirements

In TMDSC, a conventional temperature program (heating or cooling at a constant rate, or isothermal conditions) is overlaid with a small temperature perturbation (modulation). In the evaluation algorithm, it is assumed that the reaction of the sample to the conventional temperature program and the modulation to not influence each other. The underlying part (from the conventional temperature program) and the part from the modulation can then be separated. While just as in conventional DSC the underlying part of the heat flow (total heat flow) contains the entire information, the part that is generated by the modulation, only contains information about processes that can more or less follow the modulation. In all modulation techniques, the measurement conditions must be chosen so that measurement and evaluation take place under linear and almost stationary conditions. This means that the result is independent of the intensity (amplitude) of the modulation and that the total heat flow during a relevant evaluation window (period) does not change much. The quality of the measurement improves as the underlying heating rate is reduced. Especially in the analysis of melting processes, small modulations must be used because otherwise artifacts are measured, which in turn leads to the misinterpretation of results.

TOPEM® is a modern TMDSC technique that differs from conventional TMDSC with regard to the type of modulation function and evaluation. In TOPEM®, a stochastic function is used for modulation. The intensity of the modulation function is the height of the pulse. The evaluation consists of a correlation analysis of the measured heat flow and heating rate in a selectable evaluation window. [2, 3].

Total, reversing and non-reversing heat flow

In all TMDSC techniques, three heat flow components are determined from the measured heat flow. These are the total heat flow, Φ_{tot}, the reversing heat flow, Φ_{rev}, and the non-reversing heat flow, Φ_{non}. In conventional TMDSC, the total heat flow is obtained form the measured heat flow by averaging over at least one period. The reversing heat flow is determined from the modulated component. The non-reversing heat flow is given by the difference:

$$\Phi_{non} = \Phi_{tot} - \Phi_{rev} \qquad \textbf{(1)}$$

In TOPEM® the evaluation is carried out by means of a correlation analysis of the heat flow and the heating rate. This yields the component of the measured heat flow that correlates with the heating rate and another component that does not correlate with the heating rate. The non-correlating component is the non-reversing heat flow, Φ_{non}. The reversing heat flow is determined from the correlating heat flow part [3]. The total heat flow is calculated from the sum of the two quantities:

$$\Phi_{tot} = \Phi_{non} + \Phi_{rev} \qquad \textbf{(2)}$$

At first sight, this difference in approach seems relatively unimportant. In TOPEM®, however, it allows a consistency test of the measurement to be performed as described below.

Sensible and latent heat flow

In principle, the heat flow consists of two components namely the sensible heat flow, Φ_s, and the latent heat flow, Φ_l, [3,4]. The latent heat flow does not explicitly depend on the temperature but on the kinetics of the thermal event. An example is the curing reaction of an adhesive. A temperature change during the reaction cannot cause the sample to return to its initial state. It will only change the reaction rate. The sensible heat flow depends explicitly on the heating rate. An example is the heat flow into an inert sample, which is directly proportional to the heating rate. Here, the proportionality factor is the heat capacity.

Basic principles

The starting point is the description of melting and crystallization processes by means of free enthalpy given in reference [1]. A diagram summarizing this is shown in Figure 1. The red, black and green curves are the free enthalpies of the melt, the crystal and the glass. The dashed curves represent intermediate sates. The curve with the smallest free enthalpy characterizes the stable state. All other states are metastable. The system tries to achieve the stable state but is hindered by kinetic processes (e.g. nucleation). Processes occurring in a TOPEM® measurement are marked by blue ellipses or arrows in Figure 1. These are processes that occur under quasi-stable, metastable and unstable conditions:

- **Quasi-stable processes in (local) equilibrium are for example the measurement of heat capacity without another thermal event occurring.**
- **In processes under metastable conditions the system departs only slightly from local equilibrium. Examples of this are glass transitions or melting and crystallization processes close to local equilibrium conditions such as those occurring in the melting region of impure substances (see [1]). These processes can be practically reversed** through a **small change in temperature.**
- **In processes with a large change in free enthalpy, the system starts in metastable equilibrium and "drops down" into the new more stable state. The process is hardly influenced by small temperature changes. Examples are crystallization processes after a sufficiently large degree of supercooling or melting processes of crystals with superheating.**

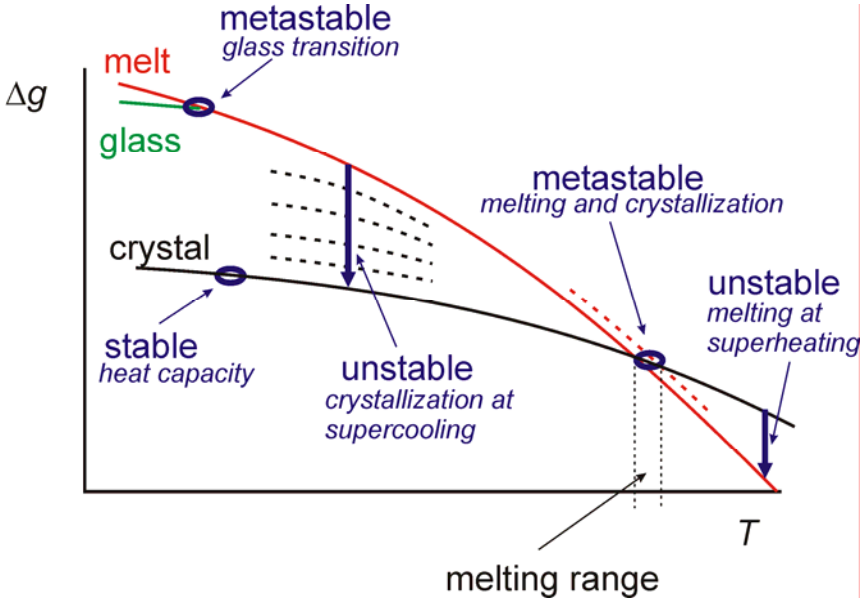

Figure 1. Schematic diagram of free enthalpy as a function of temperature. Processes are shown that occur under local stable, metastable and unstable conditions.

Description of sensible and latent heat flows

Let us assume that two different process take place in a sample that can each can be described with an order parameter, x. On melting, x, describes the degree of disorder and changes from x = 0 (ideal crystal) to x = 1 (equilibrated melt). The process with the order parameter, xme, takes place close to local equilibrium. The other process begins far way from equilibrium and has the order parameter xi. The measured heat is given by:

$$\Phi = m\, c_p \frac{\mathrm{d}T}{\mathrm{d}t} + m\, \Delta h_{\mathrm{me}} \frac{\mathrm{d}x_{\mathrm{me}}}{\mathrm{d}t} + m\, \Delta h_{\mathrm{i}} \frac{\mathrm{d}x_{\mathrm{i}}}{\mathrm{d}t} \qquad \textbf{(3)}$$

where c_p is the specific heat capacity, dT/dt is the heating rate, Δh_{me} and Δh_i are the specific transition enthalpies assigned to the corresponding processes. Since the process (me) takes place close to local equilibrium, x_{me} can follow the small temperature modulation. For this case, we can write:

$$\frac{\mathrm{d}x_{\mathrm{me}}}{\mathrm{d}t} = \frac{\mathrm{d}x_{\mathrm{me}}}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} \qquad \textbf{(4)}$$

In the non-equilibrium process (i), the order parameter does not follow the small temperature change, ΔT, determined by the modulation function. So that in this case:

$$\frac{\mathrm{d}x_{\mathrm{i}}}{\mathrm{d}(\delta T)} \approx 0 \qquad \textbf{(5)}$$

Substitution of eq (4) in eq (3) gives the measured heat flow:

$$\Phi = m\left(c_p + \Delta h_{\mathrm{me}} \frac{\mathrm{d}x_{\mathrm{me}}}{\mathrm{d}T}\right)\frac{\mathrm{d}T}{\mathrm{d}t} + m\, \Delta h_{\mathrm{i}} \frac{\mathrm{d}x_{\mathrm{i}}}{\mathrm{d}t} \qquad \textbf{(6)}$$

The first term in eq (6) is an explicit function of the heating rate. Here it is the sensible heat flow, which includes the processes that take place close to equilibrium. The latent heat flow is described by the last term. It includes processes that start far way from equilibrium.

Heat flow separation by TOPEM®

The reversing and non-reversing heat flows measured by TOPEM® can be assigned to the sensible and latent heat flow if the linearity and stationarity requirements are adhered to within the bounds of measurement accuracy:

$$\Phi_{rev} = m\left(c_p + \Delta h_{\mathrm{me}} \frac{\mathrm{d}x_{\mathrm{me}}}{\mathrm{d}T}\right)\beta_u \qquad \textbf{(7)}$$

$$\Phi_{non} = m\,\Delta h_i\,\frac{dx_i}{dt} \qquad \textbf{(8)}$$

RESULTS AND DISCUSSION

The measurements were carried out using the METTLER TOLEDO STAR^e System and the DSC823^e measuring cell with FRS5 sensor.

The materials used and the measurement conditions are specified in the respective sections.

Testing measurement conditions

Linearity

Since the evaluation methodology in TMDSC is based on the analysis of linear systems, the measurement program must be chosen so that the measured heat flow satisfies linear conditions. This is the case if the reversing heat flow is independent of the intensity of the temperature modulation (the pulse height, i.e. the amplitude). The maximum intensity depends on the material and the events to be investigated. With melting, the linearity limit is usually less than 0.1 K.

Figure 2 shows an example of a linearity test using the melting of polyethylene terephthalate (PET). Two samples of similar mass were measured with differently large pulse heights with an underlying heating rate of 0.3 K/min. The pulse heights were ±5 mK and ±50 mK. The reversing heat flow curves in Figure 2 are independent of the pulse height. The noise is however larger with the small modulation intensity. The blue curve is the difference between the two Φrev curves. This material can be measured with a pulse height of ±50 mK.

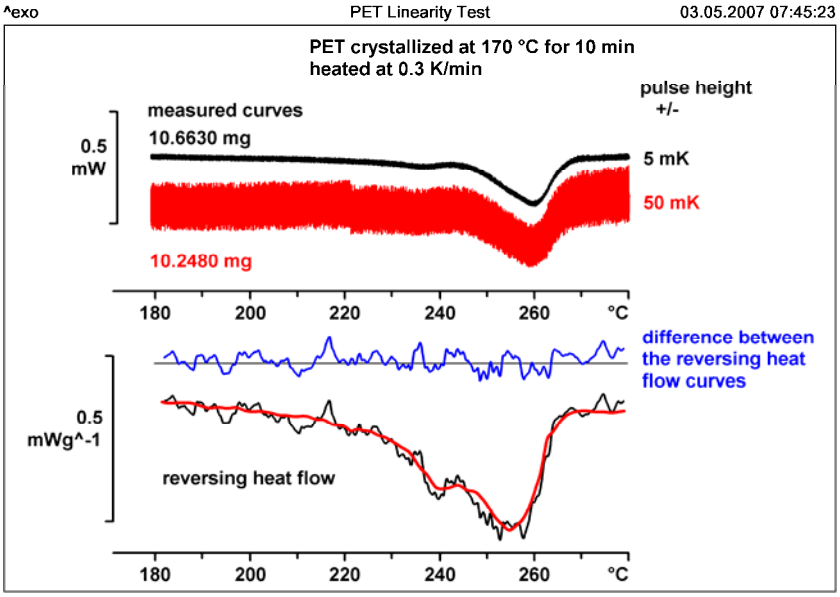

Figure 2. Test of the linearity condition using PET that had been crystallized at 170 °C. Above: measurement curves. Below: reversing heat flow and the difference between the two curves (blue).

Stationarity

The total heat flow should at the most change only slightly in an evaluation window. This condition cannot always be fulfilled particularly at higher heating rates during relatively rapid thermal events. In contrast to conventional TMDSC, TOPEM® offers the possibility to detect regions of curves in which an interpretation is critical. This is done by comparing the measured heat flow and the total heat flow. Figure 3 shows these curves in the melting region of a 40:60 mass % sucrose–water mixture. Over a wide range, the total heat flow corresponds to the mean value of the measured heat flow. In this range, the curves obtained can be evaluated both quantitatively and qualitatively. The total heat flow is however too small in the region of the peak maximum and the high temperature side of the peak. The measurement curve is primarily determined by the heat transport and less by the melting process. To obtain quantitative results with TOPEM® in this region, the heating rate must be reduced.

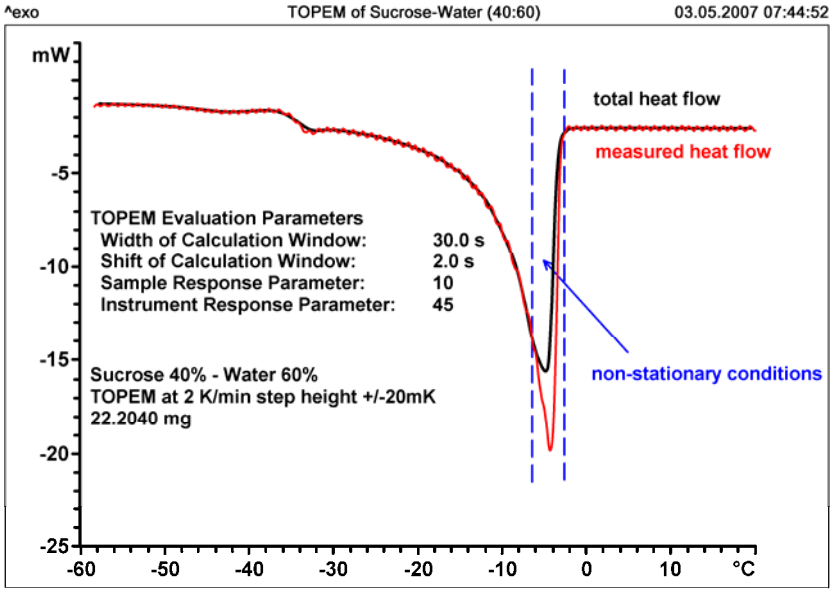

Figure 3. TOPEM® measurement in the melting region of a sucrose–water mixture.

Melting processes

When TOPEM® is applied to melting processes, several different cases have to be considered.

Melting of pure materials

Pure materials (e.g. indium) melt at the equilibrium melting temperature. During the melting process the sample temperature does not change [5] and can not therefore follow a temperature modulation. The measured TMDSC curves are mainly caused by the change in the heat transport conditions. TMDSC methods are thus unsuitable for the measurement of sharp transitions of this type.

Reversible melting close to local equilibrium

Melting processes during which crystals and melt exist in local equilibrium occur for example with mixtures that have a broad melting range. Such processes should according to eqs (8) and (9) supply a contribution to the reversing heat flow, while the non-reversing heat flow is small. The diagram on the left side of Figure 4 shows the simplified phase diagram of the sucrose–water system [10]. The path taken on heating is marked by arrows. The melting process begins at about –36 °C with the melting of small non-equilibrated crystals. This gives rise to a melt with a critical concentration of about 80 mass% sucrose. The non-reversing heat flow shows the corresponding peak. Afterward the melting process follows the liquidus line whereby crystals and melt are in local equilibrium. This part of the melting process supplies a contribution to the reversing heat flow. The melting processes that give rise to a reversing heat flow are called reversible melting and the others non-reversible melting.

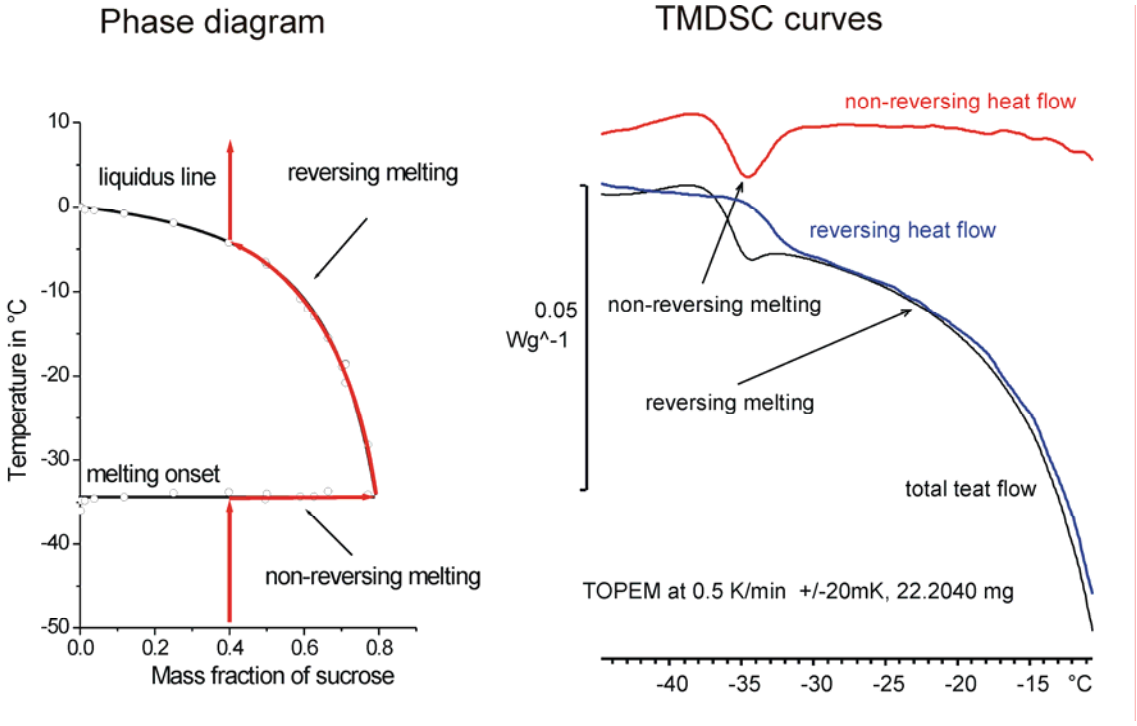

Figure 4. Left: Simplified phase diagram of a sucrose and water mixture. The path taken by the measurement is marked by red arrows. Right: Curves obtained from a TOPEM® measurement.

Non-equilibrium melting behavior: superheating of polymers

With many semicrystalline polymers, relatively stable crystallites superheat and melt above their thermodynamic melting temperature. In this situation, the melt and crystallites are not in thermodynamic equilibrium. The melting process is non-reversible. A sample of polyethylene terephthalate (PET) was first crystallized for 10 min at 170 °C. The sample was then measured using a pulse height of ±50 mK and an underlying heating rate von 0.3 K/min. The measurement curves in the region of the main melting peak are shown in Figure 5. As expected, the peak in the Φnon curve is significantly larger than in the Φrev curve.

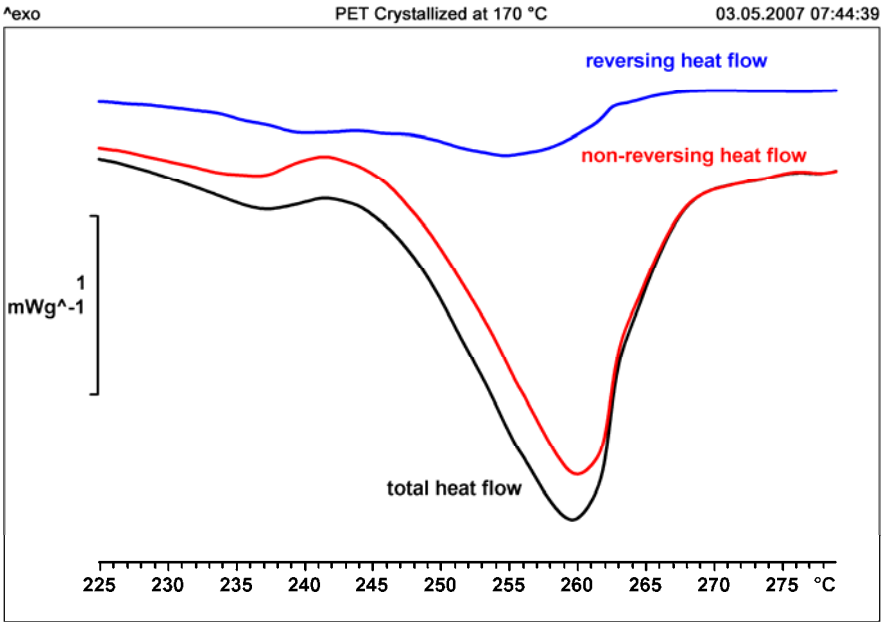

Figure 5. Heat flow curves in the melting region of PET that had been crystallized for 10 min at 170 °C. The underlying heating rate was 0.3 K/min.

Differentiation of different stable crystallites

PET crystallizes on cooling at 0.5 K/min from the equilibrated melt. In the following heating measurement at 0.5 K/min, the total heat flow curve exhibits a double peak (Fig. 6). The TOPEM® measurement shows that the reason for the double peak lies in the existence of crystallites of different stability. In the first peak, the reversing heat flow predominates. Smaller crystallites melt reversibly close to their equilibrium melting temperature. In the second peak, crystallites melt with superheating. This peak is almost entirely to be found in the non-reversing heat flow. The melting process is fundamentally different to that observed at a temperature about 10 K lower.

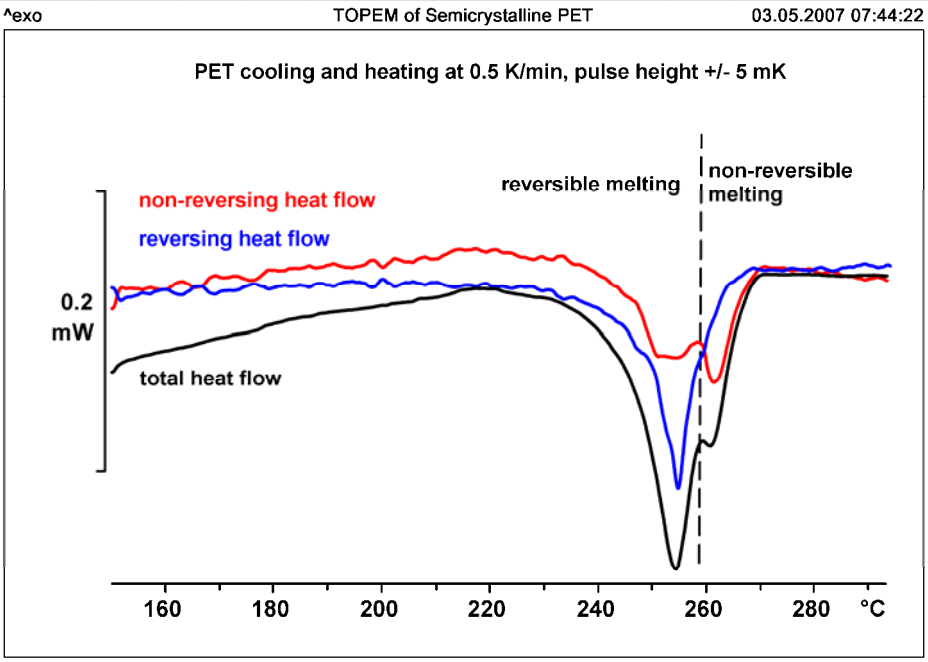

Figure 6. The melting behavior of PET that had been previously cooled at 0.5 K/min shows two different melting processes.

CONCLUSIONS

When TOPEM® is used to investigate melting processes, attention must be paid to the linearity of the measurement. The linear region is determined beforehand in trial experiments.

The range in which TOPEM® curves are valid can be established by comparing the total heat flow and the mean value of the measured heat flow.

Processes that take place under conditions of local equilibrium can be detected in the reversing heat flow because they more or less follow the temperature modulation. Processes that take place far from equilibrium do not follow the temperature modulation and thus contribute to the non-reversing heat flow.

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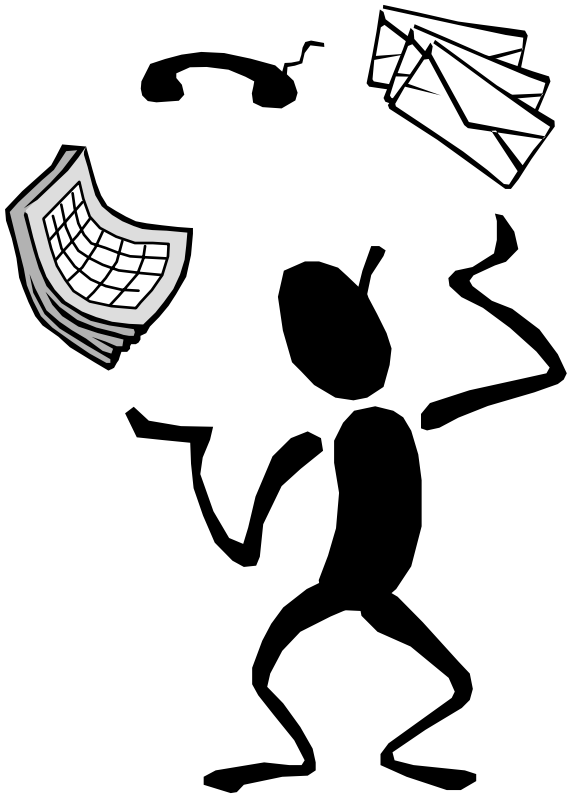

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