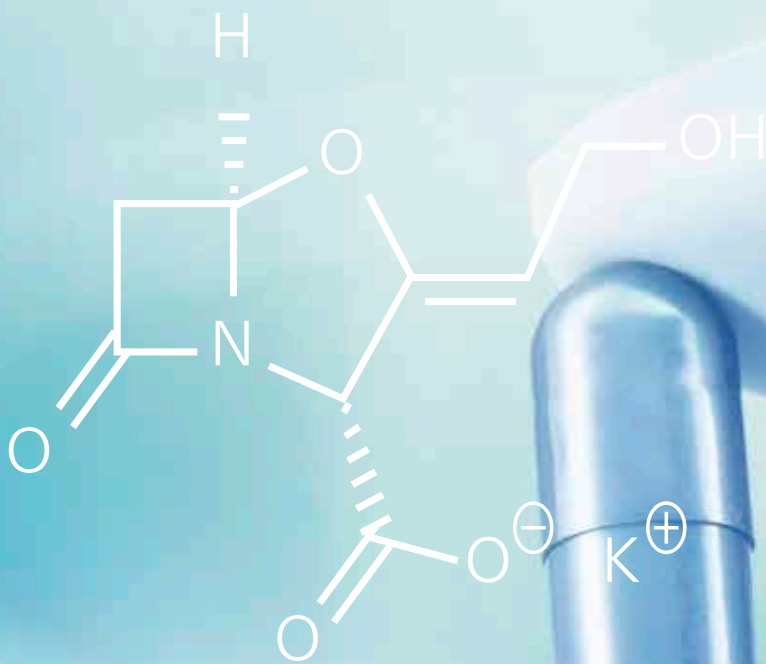


ONset

NETZSCH

CUSTOMER MAGAZINE

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NETZSCH
Goes Pharma ...

Content

- 4 COVER STORY | *Nevio* – The New Name for Thermal Analysis in Pharmaceutical Research and Quality Control
- 8 *Aëolos Quadro* : On the Search for Traces of Small and Large Gas Molecules
- 11 DEA 288 *Ionic* – Cutting-Edge Technology, Ready to Meet the Challenges of Intelligent Production
- 14 *Customers for Customers*: The NETZSCH Thermokinetics Simulation Software for the Production of TiO₂ Photocatalysts
- 18 *Tips & Tricks*: DIL/TMA – Even Special Samples Can Be Handled
- 20 Improve the Energy Efficiency of Your Company with NETZSCH Instruments
- 22 SKT 2018 – The Coupling Provides the Solution
- 23 Events
- 24 Imprint

4



11



18



23



Dear Reader:

I am happy to present to you today – in this 18th edition of the **onset** – our newest instrument series, the NETZSCH *Nevio*. Equipped with the innovative *Proteus® Protect* software development, this new generation comprising the DSC 204 **F1** *Nevio*, TG 209 **F1** *Nevio*, DSC 214 *Nevio* and TG 209 **F3** *Nevio* is especially designed for the characterization of pharmaceuticals, foods and cosmetics.

We also have something new to offer in the field of gas analysis. Continued development on our mass spectrometer has yielded real advancements in gas detection with the use of just a single software application – you can go “searching for traces” with our new *Aëolos Quadro*.

With the innovative DEA 288 *Ionic* – a complete package for investigating the curing behavior of reactive resins, even in-process – you are well prepared for the intelligent production of tomorrow in process analysis.

Under the category *Customers for Customers*, Andreas Vogel and Dr. Frank Kern from the Institute for Manufacturing Technologies of Ceramic Components and Composites at the University of Stuttgart will show you how problems in the production of TiO₂ photocatalysts can be solved by means of the NETZSCH Thermokinetics simulation software.

With *Tips & Tricks* from our dilatometer specialists, you will become an expert at sample preparation – whether it’s powders/pastes, waxes or liquids that are to be measured.

The new energy-efficient STA 449 *Jupiter® Eco* Series has been designed with a view to energy-consciousness in the laboratory – our contribution to energy and cost awareness in everyday lab work is presented on pages 22 and 23.

Last but not least, I warmly recommend the SKT 2018 – the 7th “Thermal Analysis with Evolved Gas Analysis” Coupling Days in Selb, Germany from October 16th to 18th. Take this opportunity to exchange ideas with experts and users from all over the world, whether you are already experienced at coupling techniques or have only had relatively little exposure to the field.

I wish you much enjoyment browsing through this latest issue of **onset** and hope that it will also offer you some interesting inspiration for your day-to-day work.



Dr. Elisabeth Kapsch
Director of Applications & Services



Nevio – The New Name for Thermal Analysis in Pharmaceutical Research and Quality Control

Dr. Gabriele Kaiser, Business Field Management for Pharmacy, Cosmetics, Foods



Fig. 1. TG 209 **F1** Nevio and DSC 214 Nevio

DSC and TGA are methods of thermal analysis that are already established in pharmaceutical research and industry for the characterization of the physico-chemical properties of active ingredients and excipients. This includes, for example, the detection of phase transitions, determination of the purity of substances or the analysis of compositions of substances and mixtures. Our new *Nevio* instrument line has been specifically designed to address such issues and offers many intelligent solutions in line with the requirements of 21 CFR Part 11.

Just imagine being able to command your instrument to carry out a measurement on a sample prepared by you and then having it do so completely autonomously – including evaluation of the data. All that's left for you or your superior to do is to review and approve the results. If predefined measurement conditions such as the desired atmosphere cannot be maintained because, for example, the gas bottle is empty, the system simply notifies you.

A look into the future? No! This is already a reality in the NETZSCH *Nevio* line (represented by the TG 209 **F1** *Nevio* and DSC 214 *Nevio* in figure 1).

Along with reliability and the highest of precision, the *Nevio* series offers you:

Autonomous Evaluation without Operator Intervention

All of the measurements are based on methods which can also include specifications for evaluation along with the actual measurement program. If *AutoEvaluation* is involved, this yields autonomous evaluation of the DSC or TGA curve, even if there is a different curve form each time. The algorithms behind *AutoEvaluation* are capable of detecting and assigning thermal effects. So now, even DSC curves with several endothermic and exothermic effects – often typical for crystalline organic substances – can be analyzed automatically. In order to ensure that only approved methods are employed, appropriate settings can be taken in the software.

Experienced users can employ the automatic evaluation results as a second opinion. If desired, recalculation of the values is, of course, also possible.

Simulation of Curves of Physical Mixtures

By means of the *SuperPosition* feature, users can get an impression of how DSC or TGA curves for physical mixtures look when the components are compatible with each other, i.e., do not interact with each other. Based on measurements of the individual substances, overlapping curves with freely selectable mass ratios can be calculated in the *Proteus*® software. These curves, which are generated via *SuperPosition*, can be both evaluated and included in the *Identify* libraries and used for database comparisons.

Figure 3 shows the DSC curve of a physical mixture of α -lactose monohydrate, microcrystalline cellulose and corn starch in comparison with a calculated curve additively composed of the curves of the individual components. Although small differences are always to be expected in mixtures in which the components were directly weighed into the crucibles, the two DSC profiles are in good agreement.

If other/additional effects occur, or if effects are completely missing from the measurement curve of the real mixture, this is an indication that either not all components were taken into consideration or that the components of the mixture interact with each other.

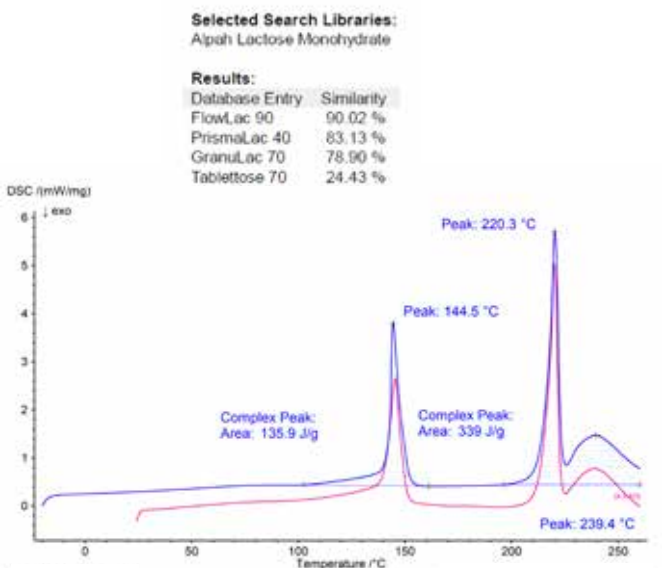


Fig. 2. DSC measurement on α -lactose monohydrate (FlowLac 90, blue) and database comparison (curve of the database entry in pink) Sample mass: 4.94 mg, heating rate: 10 K/min, Al crucible, N_2 atmosphere

Identification of Substances with Only One Click

Identify – that is the name of a curve identification and database system which is unparalleled in the world of thermal analysis. Comparison of current measurements with database entries makes it possible, for example, to determine an excipient type and thus prevent mistakes in identification. The basic version of the NETZSCH software (8th generation of the *Proteus*® software) already includes a database with more than 160 entries from the pharmaceutical, cosmetics and foods sector. The user can quickly and easily create new libraries and expand them with knowledge and experiments of their own.

Figure 2 shows the result of applying *Identify* to a measurement on α -lactose monohydrate (FlowLac 90) along with the corresponding hit list by percentage of similarity. In the case shown, FlowLac 90 leads the ranking with a similarity value of just over 90%. The associated DSC curve (database entry, pink) is graphically superimposed onto the experimental curve, allowing for an additional visual comparison of the curves.

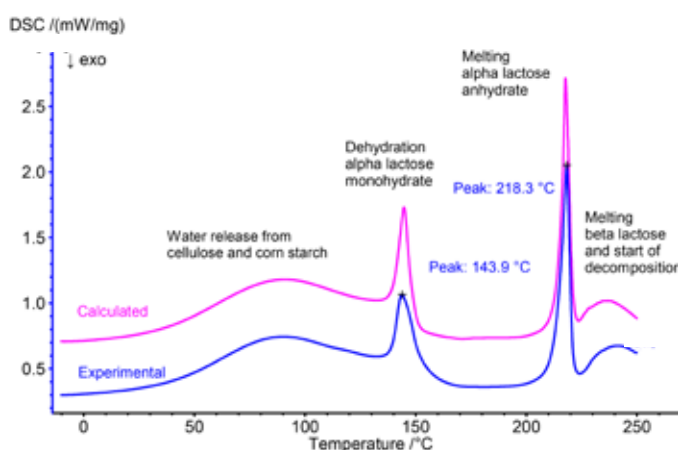


Fig. 3. DSC curve on a mixture of 36% α -lactose monohydrate, 45% microcrystalline cellulose and 19% corn starch (blue) in comparison with a curve calculated by means of *SuperPosition* (magenta); conditions of the DSC measurement: sample mass: 6.11 mg, heating rate: 10 K/min, Al crucible, N_2 atmosphere

DSC and TGA – Two Complementary Methods

DSC and TGA are listed in the Pharmacopoeia of the United States (USP), Europe (EP) and Japan (JP) as techniques for the investigation of such occurrences as melting and crystallization processes, polymorphic forms, glass transitions, the interactions between mixture components (all DSC), mass changes, the release of water and residual solvents, and thermal degradation (TGA). The content of the respective descriptions is largely harmonized. In the Japanese Pharmacopoeia, however, thermogravimetry is additionally listed as an alternative method for the determination of loss on drying and for the determination of water content (water determination) by means of the Karl Fischer Titration.

DSC and TGA are often used as complementary techniques – e.g., to allow decisions to be made as to whether an effect is based on a structural change or a mass loss. For a deeper understanding of evaporation and decomposition processes, coupling with a gas analysis system such as a Fourier-Transform infrared spectrometer (FT-IR), a mass spectrometer (MS), or a combination of a gas chromatograph with a mass spectrometer (GC-MS) is recommended.

The following example using aspartame, an artificial sweetener, shows which conclusions can be drawn from thermoanalytical measurements. Aspartame has a sweetening power 200 times that of sugar and is added to both medicines and foods. As a food additive, aspartame is designated E 951 in Europe.

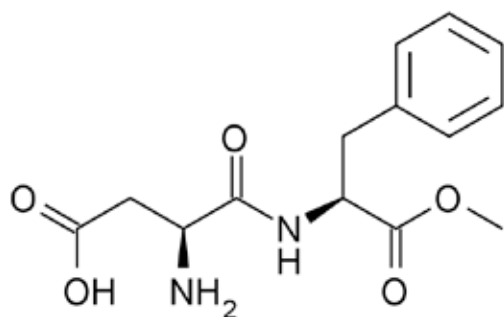


Fig. 4. Structural formula of aspartame (*N*-(*L*- α -5-aspartyl)-*L*-phenylalanine-methyl ester)

Does Aspartame Retain Its Sweetening Power during Heating?

Presented in figure 5 is the DSC curve of aspartame. A total of four effects can be seen: from right to left, these are two peaks at 247°C and 186°C (each peak temperature) and a very broad effect with two maxima at 128°C and approx. 69°C.

Comparison with a TGA measurement (figure 6) shows that the three effects in the temperature range up to approx. 200°C are due to mass changes (mass steps at 54°C, 115°C and 185°C – each DTG peaks). The fourth effect, with an extrapolated onset temperature of 243°C and a peak temperature of 247°C (figure 5), is not related to any mass-loss step and can therefore be associated with a structural transformation. These temperatures are in good agreement with the melting point of aspartame listed in literature [1] of 246°C to 247°C. It must be noted, however, that also above 200°C, the mass of the sample is still slowly decreasing. That means that melting is also superimposed by a change in the sample mass (see enlargement in figure 6), which is probably the cause of the relatively broad initial range of the DSC melting peak.

The first two mass losses are due to the release of water – both surface water and hydrate water. The TGA curve in figure 6 is very similar to the TGA curve of aspartame hemihydrate [2]. The step at 185°C (DTG peak) can be associated with the release of methanol, which is accompanied by a loss of sweetening power [3]. This means that in order to fulfill its purpose as

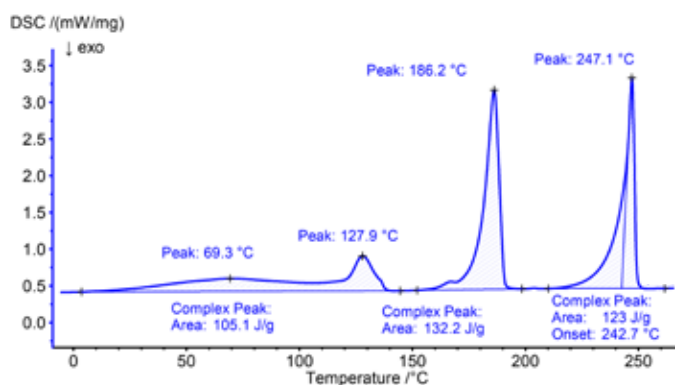


Fig. 5. DSC measurement on aspartame
Sample mass: 2.77 mg, heating rate 10 K/min, Al crucible, N₂ atmosphere

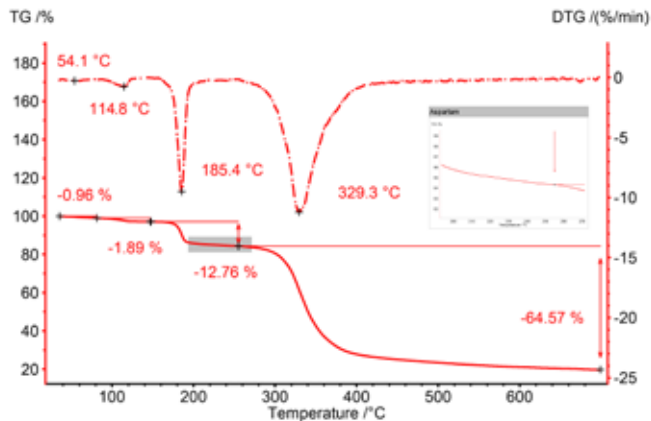


Fig. 6. DSC measurement on aspartame; presented are the TGA curve (red, solid line) and the DTG curve (derivative of the TGA curve according to time, dashed-dotted red); sample mass: 7.56 mg, heating rate: 10 K/min, open Al₂O₃ crucible, N₂ atmosphere

a sweetener, aspartame should not be exposed to temperatures above approx. 150°C.

The true strength of GC-MS coupling unfolds when many different gas components evolve at one time, as is the case for the continued decomposition of aspartame above 250°C (figure 7, DTG peak of the decomposition peak at 329°C). Due to the temporal separation, more components can often be identified than would be possible with FT-IR or mass spectrometry alone.

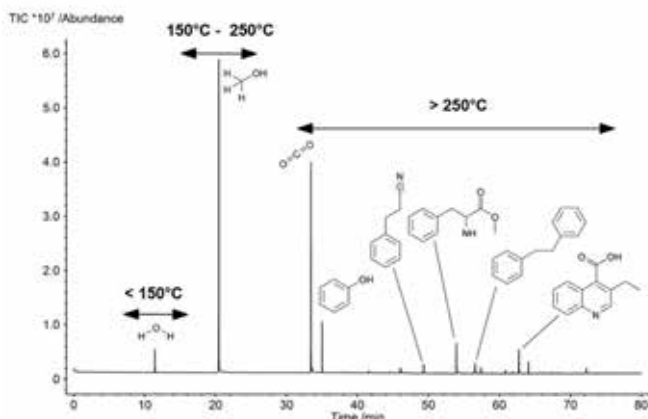


Fig. 7. Result of a TGA-GC-MS investigation conducted parallel to the other; sample mass: 7.18 mg, heating rate 10 K/min, open Al₂O₃ crucible, He atmosphere

The fact that the mass changes below 150°C are associated with water release explains the temperature differences between the DSC and DTG effects in figures 5 and 6. The TGA measurement was carried out in open crucibles while in the DSC experiment, crucibles with pierced lids were used. The larger the opening in the lid, the more the dehydration effect is shifted to lower temperatures (see also **onset**, edition 17, page 18f).

Summary

The new *Nevio* series comprises the DSC 214 *Nevio*, DSC 204 **F1** *Nevio*, TG 209 **F1** *Nevio* and TG 209 **F3** *Nevio*, offering a complete spectrum of DSC and TGA instruments for the characterization of pharmaceuticals, cosmetics and foods. As the series was specially designed for these application fields, a number of functions have been integrated that facilitate everyday work in the laboratory and provide users with possibilities for automation.

Literature

- [1] Handbook of Pharmaceutical Excipients, 6th edition, edited by R.C. Rowe, P.J. Sheskey and M.E. Quinn, Pharmaceutical Press, 2009
- [2] W.H. Hieh, W.T. Cheng, L.C. Chen and S.Y. Lin, Asian Journal of Pharmaceutical Sciences, Vol. 13, Issue 3, 2018, pp 212-219
- [3] <https://de.wikipedia.org/wiki/Aspartam>

Aëolos Quadro: On the Search for Traces of Small and Large Gas Molecules

Perfect Software Integration Makes Handling of TA-QMS Easier Than Ever Before

Dr. Carolin Fischer, Applications Laboratory

The brand new QMS 403 *Aëolos Quadro* quadrupole mass spectrometer (figure 1) features exactly the right design for capillary coupling to our TG 209 *F1 Libra* and simultaneous thermal analyzers (STA 449 *Jupiter*® series). An insulated fused silica capillary allows for the direct transfer of the evolving gases during thermal treatment into the electron impact (EI) ion source of the QMS.

All Measurements Entirely Controlled by One Software: *Proteus*®

Proteus® allows for the individual definition of any parameters relevant to TGA/STA (e.g., temperature program, heating rate, etc.) as well as any parameters relevant to MS (e.g., mass ranges, scans, etc.).

The software also handles the simultaneous start and stop of both



Fig. 1. The new QMS *Aëolos Quadro*, coupled to the STA 449 *F1 Jupiter*®

coupled systems (STA/TGA/DSC/DIL and QMS 403 *Aëolos Quadro*). During the measurement, the

thermoanalytical and MS data is displayed and stored in a single measurement file.

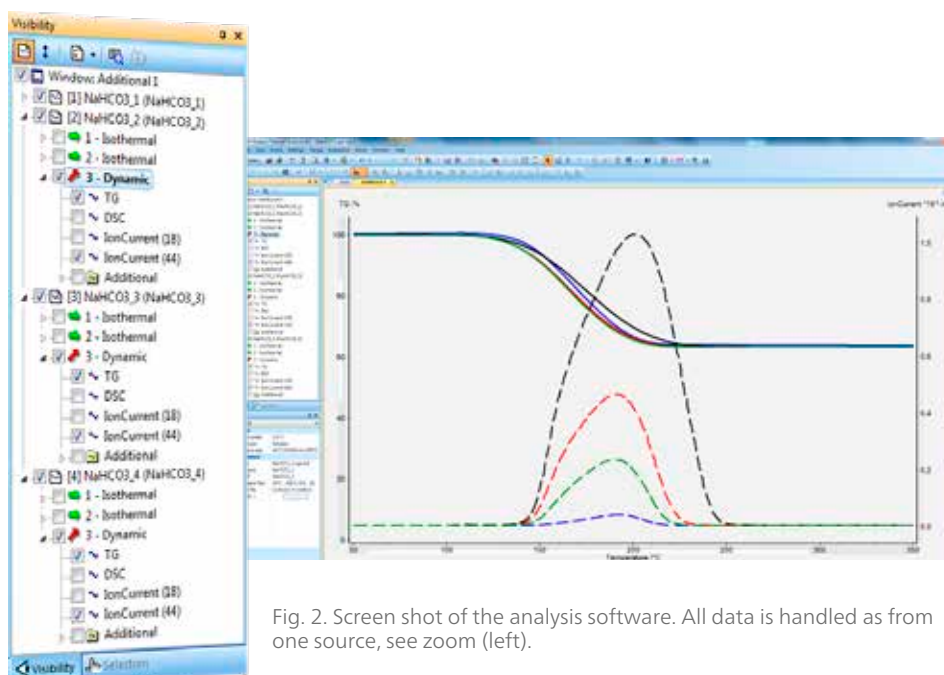


Fig. 2. Screen shot of the analysis software. All data is handled as from one source, see zoom (left).

There is no longer any need for complicated data import or switching between different applications!

Complete Integration – Also for Method-Based Analyses in ASC Operation

The software allows for programming method-based measurements and evaluation. The MS data can be monitored as scan analog (display of the envelope curve), scan bargraph (display as line spectrum), and MID with the option to select different scan bargraphs at the same time. It is possible to select the scan bargraph or scan analog with an optimized rate and sensitivity in different channels. For each position on the automatic sample changer, it is allowed to program individual MS parameters.

The Unique Software Solution

The analysis part of the software uses the single measurement file for joint presentation and evaluation, i.e., the MS results are also evaluated in *Proteus*® and are precisely correlated with the thermoanalytical results in terms of time and temperature. The MS signals can be presented as TIC (total ion current) chromatogram or individual mass numbers together with the thermoanalytical curve.

Nothing Remains Undiscovered – Navigator for 3-D, Front, Side and Surface View

The MS data can be shown in a 3-D presentation together with temperature, TGA and/or DSC signal and navigator for rotating the 3-D graphic for different views. In addition, background subtraction of a reference spectrum is possible as well as the calculation of the TIC along with the quasi-MID curves.

For quantitative evaluation of MID and QMID curves, peaks can be integrated. The software enables normalization of the spectra to a reference mass number and their exportation in an NIST-compatible format for evolved gas identification in the optional NIST spectra library.

Simply the Best Design Dedicated to Optimum Gas Flow Conditions

In developing the new coupling, we again made sure that the familiar flexibility is maintained. Standard thermal analyses as well as measurements with MS- and FT-IR-coupled devices to the STA or TGA are still possible – even under humid atmospheres.

In addition, new coupling and mass spectrometer features were implemented with the QMS 403 *Aëolos Quadro* to ensure reliable results:

- Minimized condensation losses due to a constant temperature of 300°C (optionally 350°C) throughout the entire gas transfer system from the furnace outlet to the capillary to the MS gas inlet
- No orifice, single-step pressure reduction
- Spare capillary loop at 300°C inside a furnace above the MS casing
- Very robust and service-friendly while still maintaining high sensitivity
- Upgrade of existing NETZSCH STA/TGA instruments possible

A Real Advance in Gas Detection

The QMS 403 *Aëolos Quadro* has a perfect design for gas detection up to 300 u, optionally 512 u. We were able to transfer all the advantages of the previous coupling, but we were also able to add the following new features:

- Hyperbolic quadrupole system with pre-filter
- Improved 3-D presentation of MS and thermal analysis data
- SEM with discrete dynodes and integrated Faraday cup for high dynamic range and long lifetime
- EI source with two Y₂O₃-coated filaments
- 3-D presentation of MS and thermal analysis data
- Internal reference (PFTBA) for mass scale adjustment over the entire mass range

Even the Smallest of Molecules Become Visible

The hyperbolic rod system provides improved transmission and peak separation. It shows a high transmission in the high mass range and improved sensitivity in the low mass range (H_2 , He, see figure 3). In addition, an optimized ion beam-guiding pre-filter results in a reduction of quadrupole contamination.

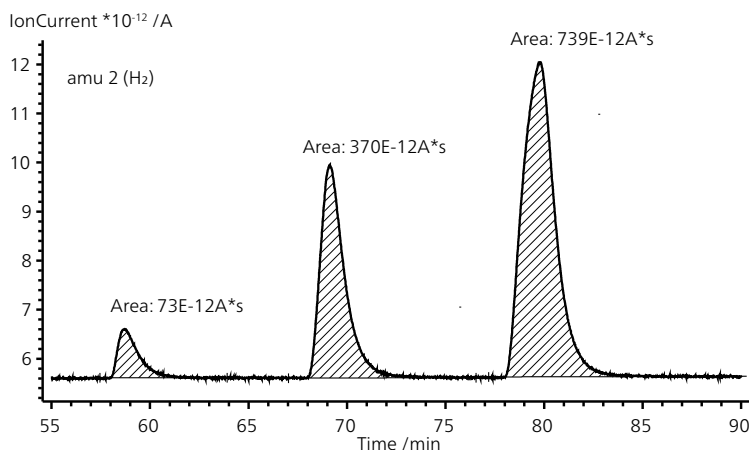


Fig. 3. STA-MS measurement of hydrogen pulses (~1, 5, 10 μ g) at constant temperature

High Detection Sensitivity Even for High Mass Numbers

Figure 4 shows a TG-QMS Aëolos Quadro measurement on polystyrene (PS granules). The 3-D presentation exhibits one mass-loss step between 300°C and 560°C. At the highest decomposition rate, styrene (m/z 104) and its dimer at m/z 208 are detected. The trimer at m/z 312 (see red circle) proves the high detection sensitivity of the QMS Aëolos Quadro.

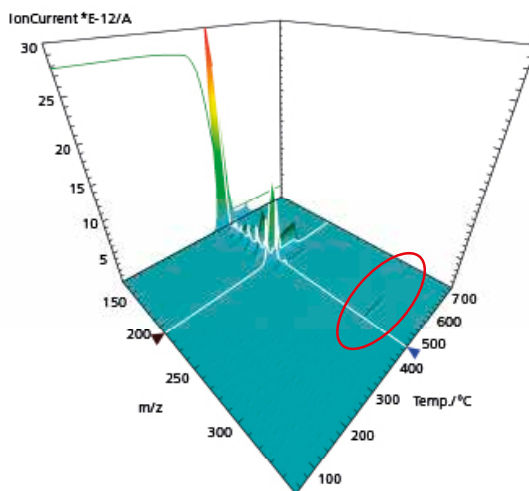


Fig. 4. 3-D plot of the measurement on PS demonstrating the TGA curve and MS results between m/z 150 and m/z 400

Conclusion

Evolved gas analysis (EGA) such as quadrupole mass spectrometry (QMS) is able to supply additional information when chemical and analytical information about products causing the mass changes are lacking.

With the new QMS 403 Aëolos Quadro, the handling of the software is considerably simplified, in fact, only one software application comes into play. All

data is treated as if from a single source. Significantly improved 3D graphics offer flexible axis display and simultaneous presentation of the thermoanalytical curve, thus facilitating evaluation and giving immediate insight into the decomposition behavior.

Please also note this year's SKT 2018 meeting all about coupling! For more information, see page 22!

DEA 288 *Ionic* – Cutting-Edge Technology, Ready to Meet the Challenges of Intelligent Production

Dr. Alexander Chaloupka, Business Field Management for Process Analytics



Fig.. 1. DEA 288 *Ionic*

Dielectric analysis – a technology that has been in use for 40 years but is not widely known. The literature agrees: Dielectric analysis, or DEA for short, has the greatest potential for characterizing the following in a process environment and thus for controlling industrial manufacturing processes:

- Material changes
- Glass transition
- Gel point
- Curing of thermosets
- Melting and crystallization of thermoplastics
- Flow behavior

The Potential Is Fully Available

Carbon-fiber reinforced plastic (CFRP) is the material with the highest potential for lightweight construction in the automotive and aerospace industries. It features excellent mechanical stability contrasted by high raw material costs. Compared to an equivalent component made of steel, however, a weight reduction of up

to 67% can be achieved. As with typical household adhesives, the plastic in which the carbon fibers are embedded must cure. If the curing of a CFRP component is not entirely completed, the specifications for its mechanical requirements are not fulfilled. However, if the processing time is actually longer than it needs to be (to allow for an unknown duration of curing), the process becomes unprofitable due to the resulting increase in unit costs.

In order for this technology to make the breakthrough to medium- and large-series production with a minimum of waste, the production processes must be intelligent and robust. This can only be achieved by continuously checking the curing state of the complex mixed material.

Particularly in carbon composites, dielectric analysis had reached its limits in the past: Due to the electrical measuring principle, contact between electrically conductive fillers such as carbon fibers and the measuring electrodes resulted in an electrical short-circuit, making a meaningful measurement impossible.



Fig. 2. Dielectric tool sensor

The Limits of What Is Technically Feasible Have Been Extended

Having understood the problems already a few years ago, NETZSCH-Gerätebau GmbH took on the challenge of redesigning dielectric analysis and raising it to a higher level.

We are proud to now be able to present a package allowing data acquisition in the mold even for polymers with electrically conductive fillers, thus enabling a self-regulating production process. The secret behind this new technology lies in an update to the electronics and a sensor design that is unique in the world and exceeds state-of-the-art. Not only do the new sensors achieve unparalleled performance in dielectric measurement, but their application range has also been significantly expanded:

- Continuous operating temperature of 300°C
- Internal pressure resistance of the mold: 300 bar
- Extremely scratch-resistant sensors due to the ceramic base material
- Thermoshock-resistant
- Resistance to solvents

This is the ideal sensor for harsh process conditions.

Real-Time Process Monitoring and Intervention

Thanks to our know-how in material characterization and the DEA 288 *Ionic* (figure 1, sensor in figure 2) as process measurement technology, NETZSCH offers the best conditions for the critical but invisible manufacturing step of analyzing CFRPs in a closed mold and

controlling the processes on this basis in real-time. To this end, sensors are installed directly in the molds. When certain characteristic values are reached, machine actions can be automatically triggered by the DEA. This results in an intelligent process yielding an optimum state of material in the shortest possible time.

Measurement, Control and Analysis Made Simple

The DEA288 *Ionic* comes standard with analog and digital interfaces for communication with production systems. In addition, with the intuitive, easy-to-use software environment in *Proteus*® 8.0, NETZSCH offers a solution which minimizes efforts for defining the measurement specification and data analysis. With the real-time "Critical Point" evaluation option, attainment of the following characteristic values is displayed during the running measurement:

- Recognition of the resin front
- Best flow behavior / Minimum viscosity
- Gel point
- User-defined degree of cure

Each of these characteristic values can, of course, be assigned to initiate a desired operation by the machine.

If a comparison of the "Critical Points" of different faultless or faulty components is required, these can be viewed jointly in the *Proteus*® 8.0 analysis software and exported in a data format of the user's choosing.

Process Analytics – A Complete Package for the Intelligent Production of Tomorrow

Intelligent production systems in the future will need to work almost independently, making decisions about the condition and progress of a component's production without user input.

In order to address such issues, NETZSCH-Gerätebau GmbH has set up the "Process Analytics" division to design the process package of the future in collaboration with partners from the processing industry. The data obtained from component analyses were hereby transmitted in real time via modern IoT (Internet Of

DEA 288 Ionic

Things) interfaces and used for communication between the individual systems and sensors that are involved in other ways.

Based on the data, pattern recognition is carried out and neural networks are set up that can map and influence a reciprocal interaction of the process-influencing parameters. To this end, the DEA 288 *Ionic* as a base will be continuously supplemented over the coming years with new features for data preparation and analysis in the currently existing *Proteus*[®] environment, and will be expanded with its own adaptive platform over the long term.

Visual Example – What Can We Learn from a Measurement Curve?

The following figure 3 shows the production of a carbon composite component based on an epoxy resin at a mold temperature of 160°C. The DEA measurement was started via a trigger signal from the hot press at the beginning of the closure process.

We see:

1. CP1: material arrival

The press is entirely closed at 0.14 min and the epoxy resin softens quickly due to the mold temperature.

2. CP2: minimum viscosity

After 0.84 min, the material reaches the state of its best flow behavior. At this point, the cross-linking process begins to dominate the dielectric signal.

3. CP3: gel point

The material's gel point is in the turning point at 1.29 min. This implies that the material is no longer capable of free flow and that the solid properties are predominating.

4. CP4: 90% degree of cure

In this example, achieving a degree of cure of 90% is decisive for the mechanical performance of the component. This dependency was determined in advance by the correlation of destructive mechanical tests on components with differing degrees of cure. From 2.21 min onward, the component meets its requirements for usability.

Log ion visc. /Ohm*cm

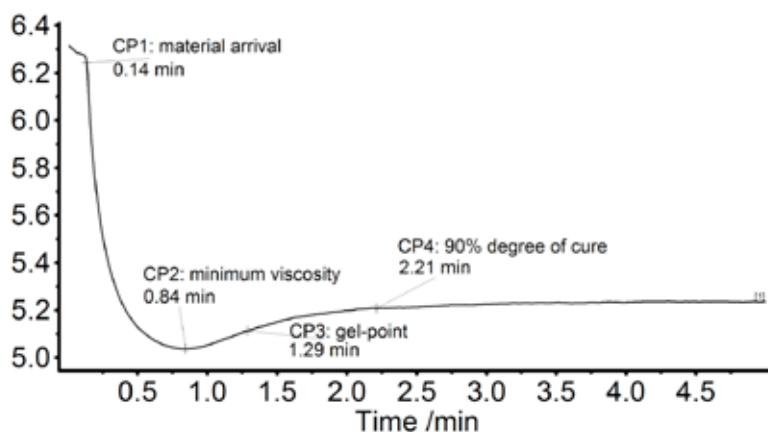


Fig 3. DEA measurement on a carbon composite component

The NETZSCH Thermokinetics Simulation Software in the Production of TiO₂-Photocatalysts

Andreas Vogel, Dr. Frank Kern, Thi Phuong Vu, Prof. Dr. Rainer Gadow

Institute for Manufacturing Technologies of Ceramic Components and Composites at the University of Stuttgart

Introduction

Increasing industrialization in the developing countries, constant world population growth and the effects of climate change place increased demands on the areas of politics, research and economy to ensure a sustainable water supply [1]. These requirements can only be met by improved water purification technology with newly developed technical procedures and products, such as photocatalysis with appropriate TiO₂ catalysts.

The principle of photocatalysis with the TiO₂ modification known as anatase, along with other fundamental investigations on the photochemical behavior and photocatalytic properties of anatase, were already published in the early 1970s [2-4].

In heterogeneous photocatalysis, UVA radiation in the range of approx. 315 to 400 nm activates the charge carriers in the TiO₂ semiconductor, leading to electron transfer across the band gap of the semiconductor. This ultimately produces free hydroxyl radicals on the TiO₂ surface, which induce redox reactions on absorbed substances. Within nanoseconds to milliseconds, organic substances are mineralized and inorganic substances are decomposed (mainly into CO₂, H₂O and N₂) by the hydroxyl radicals that are formed. Photocatalysis is thus able to remove undesired trace substances such as drug residues, industrial chemicals and herbicides from the water.

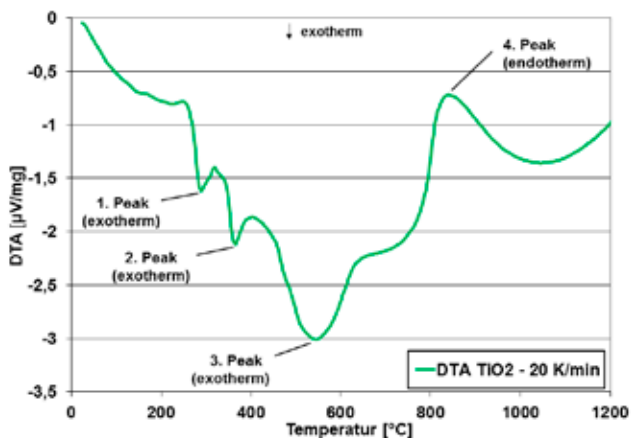


Fig. 1. DTA result for the recording of the material and phase transitions of TiO₂

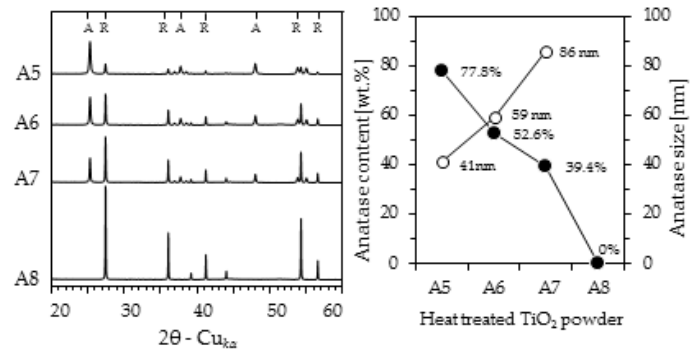


Fig. 2. X-ray diffraction pattern, amounts of anatase and sizes of the TiO₂-powders A5 - A8 (600, 650, 700 and 800°C)

To achieve high photocatalytic performance, crystalline portions of anatase and rutile are needed in TiO₂; therein, the proportion of anatase should dominate. This article describes the production of TiO₂ using a sol-gel process, thermal analysis and X-ray diffraction analysis along with kinetic modelling to find suitable heating rates and temperature ranges for production.

Experimental

For the production of TiO₂, a modified sol-gel process from [5] was applied, which initially produced a sol from the TTIP precursor (titanium tetraisopropoxide or tetraisopropyl orthotitanate, C₁₂H₂₈O₄Ti) by adding ethanol and acetone. After a gelation time of 72 hours at room temperature and 72 hours at 50°C, the gel was pulverized with a mortar and pestle and finally dried at 105°C to a constant mass. Finally, the white and still amorphous TiO₂ powders obtained this way were annealed and crystallized using various temperatures from 400°C to 800°C at heating rates of 5 K/min. The TiO₂ powders produced exhibited different coloring from dark grey to white, indicating less (dark grey) or more (white) organic substances transformed as well as different degrees of crystallization.

Thermal Analysis

The thermal analyses in air in the range from 25°C to 1200°C were carried out with an STA 409 C with differential thermal analysis (DTA) as the measuring

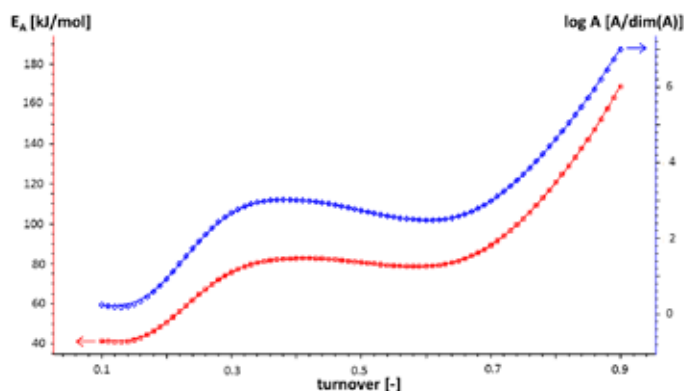


Fig. 3. Friedman-Plot: conversion rate-dependent activation energy and coefficients of impact

method since quantification of the reaction enthalpies was not intended in the scope of this work. Shown in figure 1 is the DTA analysis at a heating rate of 20 K/min. The endo- and exothermal peaks of TiO_2 represent the temperature-related material transformations. The first exothermal peak shows the split-off of the organic component of the TiO_2 precursor, TTIP. The second exothermal peak depicts the transformation of the amorphous to the crystalline TiO_2 , in which the anatase phase of TiO_2 is simultaneously formed. After the second exothermal peak, the formation of rutile begins to intensify as the thermodynamically more stable TiO_2 modification with simultaneous heat loss, which climaxes in the third exothermal peak at approx. 550°C. By the fourth peak (endothermic) at approx. 800°C, the transformation of anatase into rutile is complete.

X-Ray Diffraction

In the photocatalytic application of titanium dioxide, the purity and crystal phase play an important role. In the investigated range of 600°C to 800°C, the temperature treatment has a strong effect on the crystal phase transformation and the increase in the crystallite sizes of the powders. The results of powders A5 to A8 in figure 2 confirm this prediction.

In the diffraction patterns of the four powders, anatase and rutile were detected. At a temperature increase of 600°C to 700°C, the anatase peaks gradually decreased and have completely disappeared by 800°C. The quantification of the anatase portions is

shown as a trend in the image on the right in figure 2. With regard to the rutile phase, an increase in peak intensity was determined due to the influence of temperature. For determination of the crystallite sizes of anatase, the Scherrer equation was employed. In the range from 600°C to 700°C, anatase exhibited an increase in size of 41 nm to 86 nm. For rutile, a size of 109 nm was calculated at 600°C. At a temperature of 650°C to 800°C, the sizes were beyond the application range of the Scherrer equation.

Kinetic Modelling

For the kinetic modelling, the temperature range between 100°C and 850°C was used, which includes the relevant transformations and in which drying is already completed. The transformation from anatase into rutile, which has its reaction peak here in the form of the heat of reaction in the DTA curve as the third exothermal peak at around 550°C, should be avoided in the production of photocatalysts since it is associated with a drastic reduction in activity. The thermokinetic evaluation of the DTA data is now used to design the heat treatments (time and temperature curves) in such a way that the phase transition is largely suppressed. First, model-free estimation of the activation energy according to Friedman is carried out. For low conversion of 10%, the activation energy is at approx. 40 KJ/mol; it increases up to a conversion of 30% at approx. 80 KJ/mol. This is followed by a plateau value covering a conversion of up to 70%. Then, the activation energy rises steadily to approx. 170 KJ/mol. It can be assumed that only a single reaction occurs in the plateau range and that this partly overlaps with a second reaction with high activation energy in the range of high conversions.

In the next step, the goal is to produce an exemplary description of both main reactions by means of the anatase-rutile transformation. The two first smaller peaks cannot be kinetically modelled because they are characterized by extremely high speeds which are smeared out by heat transfer processes. In principle, parallel or secondary reaction models of nth order can be used. For the three-step parallel reaction model of nth order selected, a correlation coefficient of 99.1% can be achieved. The model is capable of resolving the last two steps well, but may not resolve the upstream processes to 400°C as expected.

Tab. 1. Kinetic parameters of the 3-step parallel reaction model

Reaction	1	2 σ	2	2 σ	3	2 σ
Coefficient of impact	2.05	0.55	52.8	7.6	1.66	0.14
Activation energy	2.14	0.47	60.2	7.9	1.5	0.2
Reaction order	5.9	0.99	154.9	18.7	1	0.12
Share (%)	20.13	12.7	58.7	13.9	21.2	N/A.

The model data is summarized in table 1. The 3-step parallel reaction model can formally be represented as:

A \Rightarrow B
 C \Rightarrow D
 E \Rightarrow F.

Reaction 2 (C \Rightarrow D) is the desired anatase-rutile transformation. The temperature must now be controlled in such a way that as little of product D as possible is produced. This can be calculated by tracking the concentration of formal reactants as a function of the thermal treatment parameters time and temperature. As examples, two heat treatment processes are successively simulated which exhibit isothermal removals at 400°C and 500°C, respectively (figure 4).

Relevant is the green curve indicating the increase in component D (rutile). As can be seen in the figures, it is predicted that the rutile content at 400°C amounts to 50% after 30 minutes. At 500°C, this value is already reached after approx. 6 minutes. A more realistic assumption for a heat treatment program is heating

at a constant speed to a certain final temperature followed by a subsequent dwell. In figure 5, heating was therefore carried out to 400°C at 5 K/min and held there; here, the green curve is again relevant for the formal reactant D. It can clearly be seen that the formation of rutile starts already in the final phase of the heating program at approx. 300°C and that an anatase portion of approx. 15% was already transformed at the beginning of the holding time. By entering different time and temperature curves, it is thus possible to pre-evaluate the heat treatment conditions. The results, however, must then be validated in detail by XRD investigations.

Summary

Kinetic modelling by means of the NETZSCH Thermokinetics simulation software allows for the time-saving determination, selection and adjustment of appropriate temperature programs that are required for process-optimized production of titanium dioxide with targeted anatase-rutile amounts in practice.

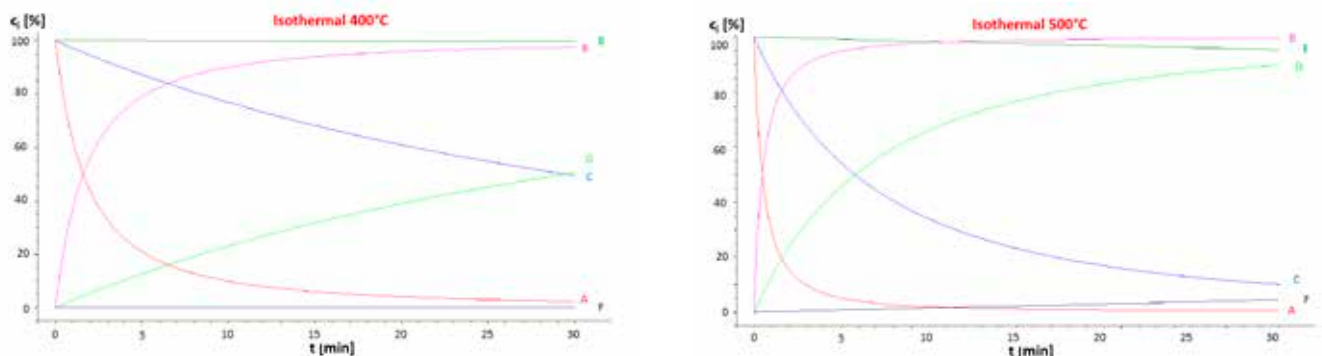


Fig. 4. Isothermal removal at 400°C (left) and at 500 °C (right)

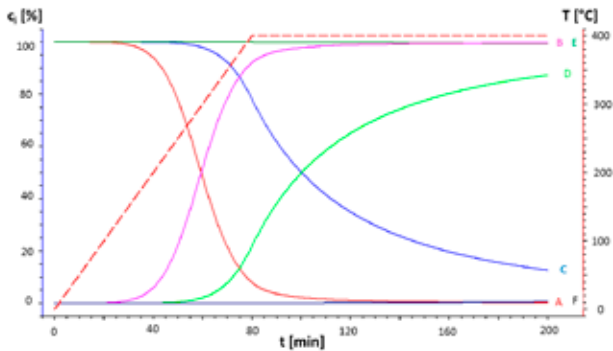


Fig. 5. Kinetic model for the targeted production of anatase-rutile amounts

Literature

[1] A.N. Grohmann, M. Jekel, A. Grohmann, R. Szewzyk, U. Szewzyk: Wasser. Chemie, Mikrobiologie und nachhaltige Nutzung. Walter de Gruyter, Berlin/New York, 2011

[2] M. Formenti, F. Julliet, J.S. Teichner: Die heterogene photokatalytische partielle Oxidation von Paraffinen und Olefinen bei Raumtemperatur mit Anatas als Katalysator. Chem. Ing. Techn. 43 (1971) 493-494

[3] M. Formenti, F. Julliet, J.S. Teichner: Heterogeneous photocatalysis for partial oxidation of paraffins. Chem Tech (1971) 680-686

[4] A. Fujishima, K. Honda: Electrochemical photolysis of water at a semiconductor electrode. Nature 238 (1972) 37-38

[5] C.-L. Wang, W.-S. Hwang, H.-L. Chu, H.-J. Lin, H.-H. Ko, M.-C. Wang: Kinetics of anatase transition to rutile TiO₂ from titanium dioxide precursor powders synthesized by a sol-gel process. Ceramics Internat. 42 (2016) 13136-13143

Main Authors



After completing his studies in Materials/ Ceramics in Apolda in 1988, **Andreas Vogel** worked in the field of construction ceramics as plant manager of Ziegelwerk Woldegk GmbH until he took up his position at the Institute for Manufacturing Technology of Ceramic Components and Composites (IFKB) in June 2000. There he has worked in the fields of the development of production methods for the production of photocatalysts, the modelling of packing densities for ceramic raw materials and mixtures, and the development of activated carbon detection methods, mercury pressure porosimetry and thermal analysis.



PD Dr. Frank Kern studied Chemistry at the Technical University of Karlsruhe and received his

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Since 2000, he has been Head of the High-Performance Ceramics Department at the Institute for Manufacturing Technologies of Ceramic Components and Composites (IFKB). His current research focuses on the development of new materials and production processes for high-performance ceramics. In 2014, he completed his postdoctoral lectural qualification on the topic "New Oxide Ceramics and Nanocomposites for High-Performance Applications" and is now an associate professor in the fields of ceramics, composites and carbon materials.

DIL/TMA – Even Special Samples Can Be Handled!

Doreen Rapp, Applications Laboratory



Fig. 1. Sample container of SiO_2 , Al_2O_3 , sapphire and graphite

Introduction

The measurement of solid samples is generally no particular challenge for the methods of dilatometry (DIL) and thermomechanical analysis (TMA). It gets more difficult, however, if the samples are powders, pastes or liquids or if the sample changes from the solid to the liquid state during the measurement. In the following, techniques will be presented enabling measurement on such samples with a dilatometer or TMA. Additionally, the points to be considered during preparation of such samples will be discussed.

Container for Powders and Pastes

Various sample containers are available for the measurement of powdery or pasty samples with the DIL

and TMA (see figure 1). They are made of SiO_2 , Al_2O_3 , sapphire or graphite. The choice of container material depends primarily on the temperature range of the measurement. Furthermore, possible interactions between the sample and container material must be taken into account.

Prior to preparation, the container including the pistons is first weighed empty and the lengths of the pistons and cylinder are determined. Afterwards, a piston is pushed into the cylinder so that it is flush with the lower edge. The container is then placed on this side. Now, it is filled from the side that is open at the top until the material is heaped slightly over the edge. For powders, it is recommended that the container be tapped occasionally during filling in order to prevent the occurrence of any cavities within the sample material. The excess is then removed with a straight edge (e.g., razor blade) and the second piston is pushed into the cylinder from above until the lower piston pokes out slightly. The lower piston is then also the one in contact with the pushrod. Now, the total length and mass of the cylinder with sample and pistons are determined. The sample length is then obtained by subtracting the lengths of the two pistons. Care must be taken that samples are prepared so as to have similar mass and length. This ensures that the samples will have a similar bulk density. In general, however, it is recommended – if the sample and the measuring task both allow for it – to press the powder into a pellet.

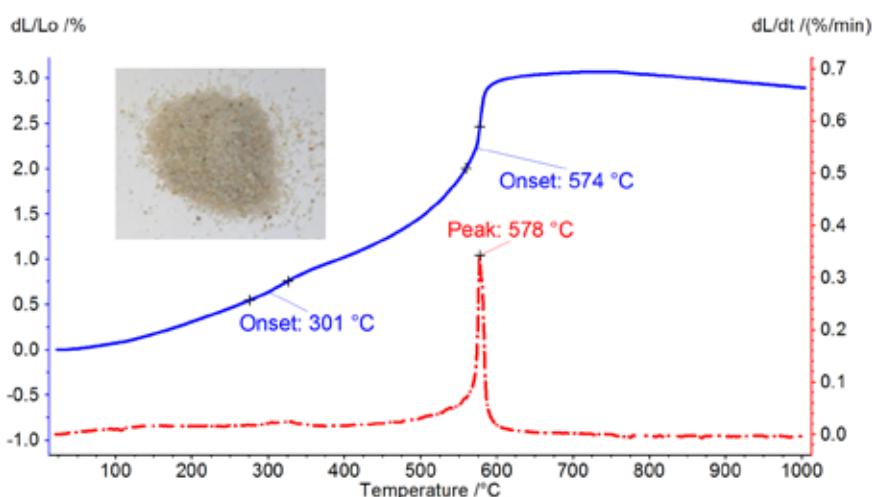


Fig. 2. Thermal expansion (blue) and rate of expansion (red) of a foundry sand (inset), measured in an Al_2O_3 container (RT to 1000°C at 5 K/min, in air)

Figure 2 shows an example of a measurement on a powder sample in an Al_2O_3 container. Here, a foundry sand sample was heated from room temperature to 1000°C at 5 K/min. At 301°C (extrapolated onset), a slight bend in the thermal expansion can be observed, which might be due to the burnout of organic components. The α - β transition of quartz can clearly be seen, with a maximum in the expansion rate at 578°C.

Tips & Tricks



Fig. 3. Al_2O_3 crucibles and discs for measurement of powders with the TMA



Fig. 4. Steel container for the measurement of waxes

For the filling of pasty samples, such techniques as injection can be used. To prevent the formation of air bubbles in the sample during filling, the tip of the injection nozzle is initially positioned at the bottom of the container and then slowly pulled upward as it empties. Here also, the container is filled until it is slightly heaped over the top, and the excess is then removed with a straight edge. The remainder of the procedure is then the same as described for the powder samples.

Due to its vertical design, the TMA also offers another measurement option. Here, the powder can be filled into a crucible and covered with a disc (see figure 3). Here, too, the same masses and filling levels should be set, if at all possible.

Waxes

For the measurement of the thermal expansion of waxes into the melting range, NETZSCH offers a steel container. This consists of a steel cylinder, a cap and a diaphragm. First, the depth of the steel cylinder is determined since this will be equal to the later sample length. To fill the container, smaller pieces of wax will be melted within the container little by little, until it is over-filled (above the edge) after the wax has cooled (see figure 4). Then, the excess is cut off with a sharp razor blade. Melting can be carried out with a hot-air gun or a hot plate. This method, however, is only suitable for samples that do not undergo change as a result of the procedure described above.

Liquids

Liquids must be enclosed in a container to determine the thermal expansion. There are two possibilities here, and the appropriate choice depends heavily on the viscosity of the sample to be measured. For viscous samples (similar to honey), the same container can be employed as described beforehand for powdery and pasty samples. Care must be taken, however, to verify that the sample will not become significantly less viscous during the course of the measurement, since the sample could then leak out of the container. In order to prevent the occurrence of any damage to the sample holder, such substances should be tested beforehand in a separate furnace when in doubt.

For samples with low viscosity, the same steel container as is used for measurements on waxes can be utilized. In this case, however, only comparative measurements are possible, and no absolute determination of the thermal expansion may be carried out, since it is not possible to correct for the expansion behavior of the container. This, however, is rather insignificant in consideration of the heavy expansion of waxes during melting.

Improve the Energy Efficiency of Your Company with NETZSCH Instruments!

Alexander Frenzl, Business Field Management for Glass, Ceramics and Building Materials



The new STA 449 Jupiter® Eco Series

* When using the instrument 3 times a day on 250 days a year

Technical Improvements with a View to the Introduction of an Energy Management System in Accordance with ISO 50001

Have you heard of "energy management"? Or are you at a company that successfully implements an energy management system? Then ISO 50001, designed to help organizations and companies with systematic energy management, should be well known to you.

In the future, the practice of an energy management system will be the basis for you, as an entity within the

manufacturing industry, to be exempted from electricity and energy taxes in certain countries such as Germany.

Systematic energy management requires that you – as a company – evaluate:

- your energy consumption
- your energy sources
- and energy use.

To optimize your energy consumption, you need to measure it and systematically improve it through organizational and technical measures.

How Is NETZSCH Involved with ISO 50001?

At the NETZSCH-Gerätebau GmbH headquarters in Selb, we introduced an energy management system in recent years. It made us aware that the energy consumption in our application laboratories and our final inspection department was high.

So in optimizing our processes, we thought: Why not allow our customers all over the world to benefit from the changes we make?

"STA Jupiter® Eco Series" – Energy-Efficient STA for Energy-Conscious Laboratory Use!

Simultaneous Thermal Analysis (STA) has been growing increasingly popular for years. It combines the two best-known methods of thermal analysis into a single device: A highly sensitive thermobalance (TGA) and a differential scanning calorimeter (DSC) are combined to show us when mass loss (TGA) or energy conversion (DSC) occur in a material. These events provide us with information about the temperature at which and duration of which, for example, a binder degrades in a ceramic material. Also, the analyses show us when a material melts and how much energy it absorbs until it is completely melted.

In general, STA will help you in the combined study of:

- Material compositions
- Thermal stability
- Phase transitions (phase diagrams)
- Binder removal and much more.

In order to ensure that an instrument of this type has the required temperature stability in application temperatures of up to 2400°C, manufacturers generally employ thermostating by means of a water cycle. The water at constant temperature flows from a thermostat through the balance chamber and sections of the furnace to keep the high-precision balance system at a constant temperature. Continuous cooling with the thermostat switched on requires a lot of energy and produces waste heat, which must be regulated by air conditioners. Thus, the energy consumption of an STA is composed of the primary energy demand for operating the system and the connected furnace(s) along with the primary demand required for operation of the thermostat. Secondary energy requirements include, for

example, air conditioning for the space in which the instrument is installed as well as water consumption.

We took a closer look at these circumstances at NETZSCH and developed the STA 449 *Jupiter® Eco Series* based on our findings. It achieves very high performance without the need for a thermostatic water circulation system.

The fact that no thermostat is needed significantly reduces energy consumption. The heating foil, which replaces the thermostat, only requires 10% of the energy used by a thermostat – so in our case, with approximately 9 STA devices in the applications laboratory, this translates to a savings of € 80,000 (based on current energy costs in Germany) over a life cycle of 10 years.

Thermostating an STA system with a water cycle costs about € 1,000 of electricity per year in Germany. In the STA 449 *Eco*, the temperature-sensitive regions are stabilized with a resistance-heating foiling, which consumes only around € 100 per year (calculation basis: Germany). For a period of use of 10 years, you thus save about € 9,000 at the instrument alone – on top of that come all the savings in the areas of water cooling, maintenance and repair.

Since the cost of air conditioning a laboratory depends on how many heat sources are in the room, this cost component is much more difficult to estimate. A thermostat is responsible for about 20-30% of the total energy required, though, and produces a major amount of the waste heat for an STA system. So we can say that the waste heat for a single STA in a room is reduced by about one third thanks to the alternative thermostating.

With the heating foil in the upper section of the weighing chamber, none of the maintenance and repair work usually required for thermostat operation (e.g., blocked filter systems) is necessary any longer.

Additionally, the heating-foil solution saves space due to the fact that no thermostat is needed in an often overcrowded laboratory. None of the STA's well-known properties are affected by the heating foil.

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Even Difficult Application Issues Can be Solved



Four Decades of Coupling

It has been over four decades since the first hyphenated techniques for thermoanalytical instruments were introduced worldwide. Growing interest and increasing demand drove the development of superior coupling solutions, bringing the applied sciences a great step forward and achieving a solid foothold for them in both R&D and industrial applications.

The Forum

The 7th SKT 2018 provides a forum for scientists to present their latest research results specifically obtained by using mass spectrometry (MS), FT-infrared spectroscopy (FT-IR) and/or gas chromatography with mass spectrometry (GC-MS) coupled to thermal analysis. The coupling

days will offer a platform for exchanging tips and tricks on sample preparation, experiments, and evaluation in lively discussion. It will, however, provide food for thought to those participants who are not yet very familiar with hyphenated techniques.

The Program

Renowned speakers from all over the world will present a summary of the state-of-the-art in coupling techniques and their applications; e.g., the degradation of natural and synthetic polymers, failure analysis of polymers, decomposition of inorganic materials, understanding of gas-phase equilibria, thermal stability of thermoelectric materials, thermal treatment of ionic liquids, SO₂ mitigation in refinery applications, alkali properties and behavior

in heated coal ashes, investigations of outgassing in oil shales, energy and powder plant development, astrobiology and more.

For the program, information on location and registration, please visit the website:

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Your SKT Organization Team

Events

Trade Fairs

	Date	Location
Rubber Expo 2018	Oct 9 - 11, 2018	Louisville, KY, USA
MS&T 2018	Oct 14 - 18, 2018	Columbus, OH, USA
SICEMAT 2018	Oct 15 - 19, 2018	S. José dos Campos, Brazil
TestXpo 2018	Oct 15 - 16, 2018	Ulm, Germany
IFAI & CAMX	Oct 15 - 18, 2018	Dallas, TX, USA
Foam Expo Europe 2018	Oct 16 - 18, 2018	Hanover, Germany
glasstec 2018	Oct 23 - 26, 2018	Dusseldorf, Germany
Analytica China 2018	Oct 31 - Nov 2, 2018	Shanghai, China
Chemplast Expo 2018	Nov 6 - 8, 2018	Madrid, Spain
Composites Europe 2018	Nov 6 - 8, 2018	Stuttgart, Germany
JEC Asia 2018	Nov 14 - 16, 2018	Seoul, South Korea
plastic 2018	Dec 5 - 7, 2018	Makuhari, Japan
P-MEC 2018	Dec 12 - 14, 2018	New Delhi, India

Conferences

	Date	Location
International Nuclear Engineering	Oct 4 - 5, 2018	Manchester, UK
JEMP 2018	Oct 8 - 10, 2018	Nantes, France
SECV	Oct 8 - 11, 2018	Barcelona, Spain
National Congress on Chemistry	Oct 12 - 13, 2018	Bologna, Italy
NuMat 2018	Oct 14 - 18, 2018	Seattle, WA, USA
GCC 2018	Oct 16 - 17, 2018	Galveston, TX, USA
Korean Chemical Society 2018	Oct 17 - 19, 2018	Daegu, South Korea
ICMSEP 2018	Oct 25 - 27, 2018	Tagaytay City, Philippines
AMI Oil and Gas Non-Metallics 2018	Oct 30 - 31, 2018	London, UK
ICEAN 2018	Oct 30 - Nov 2, 2018	Newcastle, Australia
Advanced Engineering 2018	Oct 31 - Nov 1, 2018	Birmingham, UK
CBCIMAT 2018	Nov 4 - 8, 2018	Foz do Iguacu, Brazil
PPS Americas Boston 2018	Nov 5 - 9, 2018	Boston, MA, USA

Webinars

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NETZSCH

Leading Thermal Analysis ■

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