

OnSet⁴

News, Facts and Professional Solutions for Thermal Analysis

Highest Flexibility and Performance:

The New STA 449 *Jupiter*[®]

Dr. Alexander Schindler, NETZSCH Applications Laboratory

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NETZSCH GEFTA Award 2008 to Erwin Kaisersberger



Fig. 1. The new NETZSCH STA 449 *F1 Jupiter*[®] with double furnace hoist and two furnaces

Simultaneous Thermal Analysis (STA) constitutes the simultaneous application of two or more thermo-analytical methods to one sample. The term is most often used in reference to the simultaneous measure-

ment of the mass changes and energetic effects on one and the same sample while being subjected to a controlled temperature program. Such an STA apparatus offers several advantages.



Editorial

Dear Reader:

Today we would like to present you with the latest issue of our OnSet magazine. Some of the highlights include extremely interesting articles by our customers and an introduction to various new instrument and software products launched by our development team over the past few months.

The instruments presented for simultaneous thermal analysis (STA) and differential scanning calorimetry (DSC) are full of features which open up a whole new world of possibilities in material characterization. Details can be found in the articles by Dr. Alexander Schindler from our applications laboratory. Combining the new measurement technique with component kinetics can add even more depth to the analyses. After having read through the various articles, you will see why our new instruments and software are already generating such enthusiasm

in our applications laboratories and among their first customers.

In addition to the articles about our own innovations, we have again been lucky enough to have some of our renowned customers contribute articles as well. As a physicist, I must admit that the term "cuticula of isopods" did not mean much to me until now. Thanks to the article by Dr. Frank Neues and Prof. Matthias Epple, I now not only know what a cuticula actually is, but also know that it is relatively easy to characterize one by means of thermogravimetry.

Dr. Dirk Walter's work on nano-scale dust samples gives fascinating insight into the use of TG-FTIR in environmental analysis. The methods of thermal analysis provide a well-grounded scientific basis for the study of this topic, which has been getting detailed media coverage lately.

The article by Dr. Yu Hui-Mei proves that China is capable not only of organizing major sports events like the Olympic Games, but also of holding a number one position in the research of ceramic nano-

materials. We are especially pleased that, in addition to STA-MS coupling, *PulseTA*[®] can also contribute to a better understanding of reaction processes.

We truly hope that this new issue of OnSet will again provide you with some inspiration for your work with NETZSCH instruments.

Seldom before have the topics been as diverse and exciting as in this issue.

Dr. Jürgen Blumm

Managing Director
Sales, Applications & Marketing

Continuation Page 1

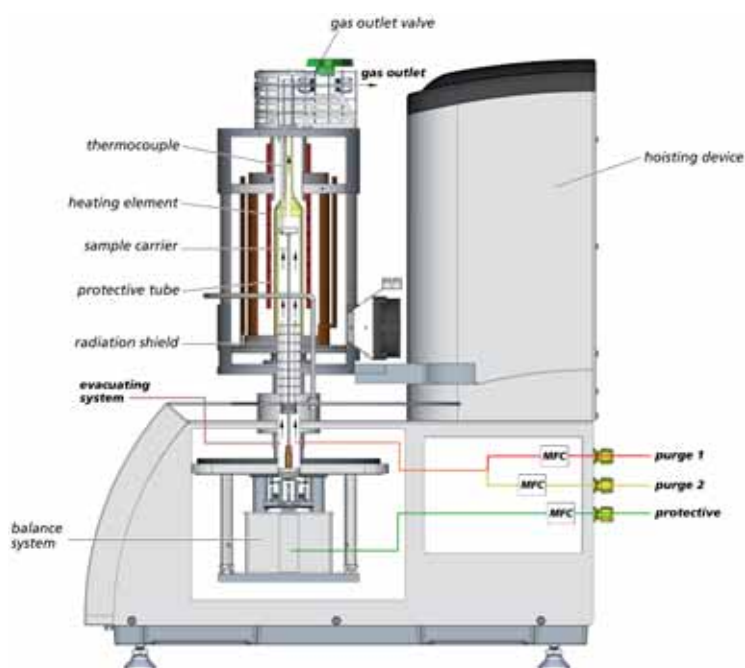


Fig. 2. Cross-section of the NETZSCH STA 449 *Jupiter*®

First of all, both the temperature-dependent mass changes and the caloric effects can be determined in a single measurement. This is far more efficient than conducting two individual measurements with a separate thermogravimetric instrument (TG) and differential scanning calorimeter (DSC).

The STA method can therefore save a lot of time. Also, less sample material is required, which can be a great advantage if it is expensive and difficult to produce. In addition, the TG and DSC results of an STA measurement can be truly compared and correlated, since the measurement conditions are identical and no possible differences in sample preparation need to be taken into consideration. This is a decisive advantage, particularly in cases

where sample material is inhomogeneous or measurement results might be influenced by the sample amount.

The simultaneous measurement of TG and DSC is also advantageous for another reason: in order to carry out an exact enthalpy determination by means of the DSC signal during a phase transition, one must have precise knowledge of the effective sample mass.

The new STA 449 *Jupiter*® combines these advantages with superior flexibility and performance. A variety of applications in fields such as ceramics, metals, plastics, pharmaceuticals and composites can be covered over a broad temperature range (-150 °C to 2000 °C), including temperature stability, decomposition, composition,

phase transitions, specific heat, etc. Its proven top-loading, vacuum-tight construction and its new, extremely precise weighing system with long-term stability make the STA 449 *Jupiter*® a very helpful tool for the thermal analysis of materials in research, development and quality assurance.

A great variety of standard and optional accessories are available, including various furnaces which can be easily interchanged by the operator (or the optional swiveling double hoist for two furnaces), sample carriers (TG, TG-DSC, etc.), an automatic sample changer (ASC) for up to 20 samples, and a variety of crucibles in different forms and materials. By means of an additional MS- and/or FTIR coupling, the STA 449 *Jupiter*® can even be used for chemical analysis.

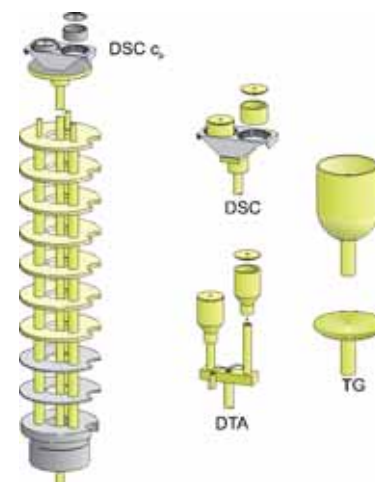


Fig. 3. Diagram of various sensor types for the STA 449 *Jupiter*®

Design and Features of the STA 449 Jupiter®

Figure 2 shows a diagram of the new STA 449 Jupiter®. The instrument has a top-loading design, i.e. the furnace is driven by a motorized furnace hoist from the top down to the sample carrier, which is positioned vertically on the balance. This principle guarantees easy handling of the sample and a long service life for the sample carrier. Gases evaporating from the sample during heating rise to the top chimney-style and can either be released from the instrument there or be channeled into an optional MS or FTIR spectrometer. Contamination of the sample carrier is prevented and the low purge gas rates necessary of approx. 50 ml/min cause only slight dilution of the sample gases, thus yielding high MS or FTIR signals.

The vacuum-tight design of the system makes it possible to conduct measurements under defined gas atmospheres: the STA apparatus can be evacuated down to $<10^{-4}$ mbar and then be refilled with a pure inert gas (Ar, N₂, etc.). This process can optionally be set up to run automatically via the software (*Autovac* function).

The weighing system is located in the vacuum-tight housing in the lower area of the measurement part. The STA 449 Jupiter® **F1** and **F3** models feature digital resolutions over the entire measuring range of 25 ng and 1 µg respectively, and the maximum sample masses are 5 g and 35 g. The housing of the balance is thermostated in order to achieve a high reproducibility and long-term stability in µg/hour.

The various furnaces and sample carriers of the STA 449 Jupiter® can easily be changed by the operator. A

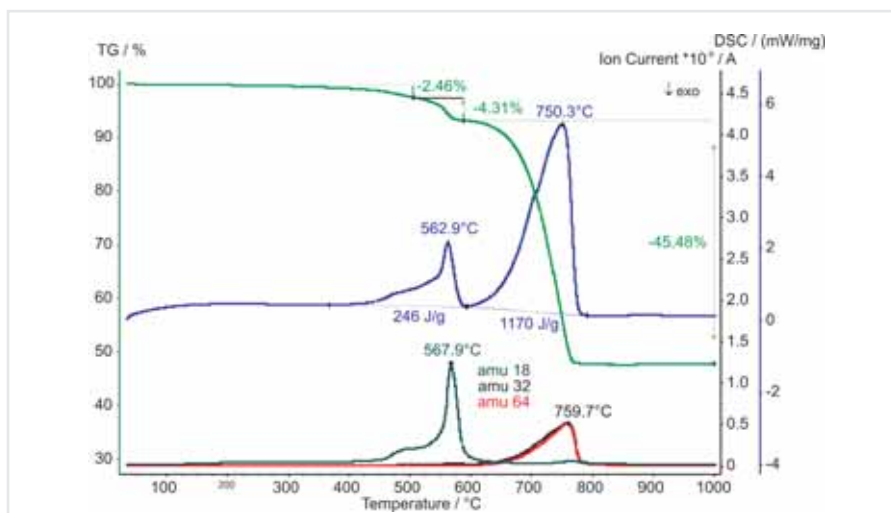


Fig. 4. Mass change (TG), heat flow rate (DSC) and mass spectrometer curves (mass numbers 18, 32 and 64) of an Fe(OH)SO₄ sample, measured with the STA 449 **F1** Jupiter®

temperature range spanning -150 °C to 2000 °C can be covered, and a water-vapor furnace for humid atmospheres (up to 100 % humidity) is also available. A swiveling double furnace hoist for two furnaces and an automatic sample changer (ASC) for up to 20 samples are available, allowing measurements to be carried out during the night or over the weekend.

The various TG, TG-DTA and TG-DSC sensors allow for easy and flexible optimization of the system to a great variety of applications. The individual sensor types are depicted in figure 3. For large sample volumes, TG sensors with plates or special large crucibles (up to 5 cm³) are available. TG-DTA sensors can be used for qualitative analysis and TG-DSC sensors for quantitative analysis of caloric effects and specific heat. These metallic sensors (TG-DSC) provide a stable and reproducible baseline, high sensitivity, an optimal signal-to-noise ratio and a short time constant over the entire temperature range. This allows for highly accurate quantitative analyses of phase transitions, even at tem-

peratures far above 1000 °C. Unique in the field of STA is the temperature-modulated DSC (TM-DSC, not available in North America and Japan). "DSC Correction" ensures that the influences of the time constant and the thermal resistance are corrected.

Application examples

Shown in figure 4 are the STA-MS results for an Fe(OH)SO₄ sample. This is a base material for the production of iron oxide particles. Iron oxide is used in applications such as color pigments and magnetic storage media. Ferrofluids contain superparamagnetic iron oxide nanoparticles, which are used as a contrast agent in MR imaging. The sample ($m_0=30.58$ mg) was measured in an N₂ atmosphere (70 ml/min) at a heating rate of 20 K/min. Platinum crucibles with pierced lids were used. Below about 600 °C, the STA-MS measurement shows a two-step mass loss which can be attributed to the separation of H₂O with a mass number of 18. Between 600 °C and

800 °C, the separation of SO₂ with a mass number of 64 and O₂ with a mass number of 32 can be seen. The end product is Fe₂O₃ (hematite). During the mass-loss steps, the DSC signal shows two endothermal effects with enthalpies of 246 J/g and 1170 J/g.

The STA measurement depicted in figure 5 shows the combustion of linoleum. Linoleum was developed as a building material in 1863 and is used primarily as a floor covering. It is robust and has an insulating effect even when it is not very thick. The linoleum sample ($m_0=5.52$ mg) was measured in air (70 ml/min) at a heating rate of 10 K/min in Pt crucibles.

The result reflects the natural components of linoleum: after the evaporation of humidity under about 150 °C, the stepwise, strongly exo-

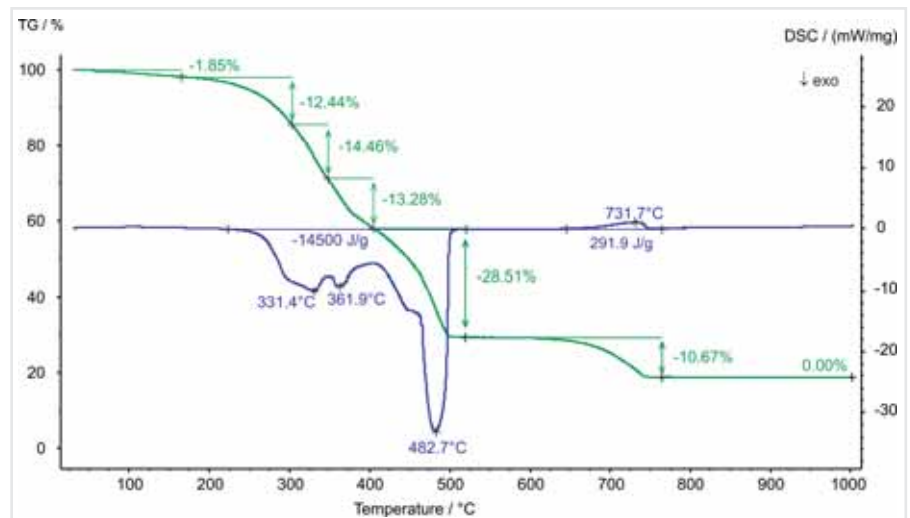


Fig. 5. Mass change (TG) and heat flow rate (DSC) of a linoleum sample, measured with the STA 449 **F3** Jupiter®

thermic combustion of linseed oil, natural resins, cork and wood flour, and the carrier material jute takes place between approx. 200 °C and 500 °C; the entire energy of combustion amounts to 14.5 kJ/g.

Between 600 °C and 750 °C, the endothermal decomposition of the filler CaCO₃ (chalk) takes place. Above 750 °C, the sample mass remains constant.

New Management Team



Dr. Thomas Denner and Dr. Jürgen Blumm

On July 1st, 2008, Dr. Otto Max Schaefer, Managing Partner of the NETZSCH Group, resigned from his interim task as Managing Director for Sales, Marketing, Services & Applications at NETZSCH-Gerätebau and introduced Dr. Jürgen Blumm as his successor. In his farewell speech during the International Sales Meeting at the beginning of July in Selb, Dr. Schaefer looked back on his exciting and interesting time at NGB with a wide array of emotions.

Dr. Jürgen Blumm (39), born in Königshofen, Bavaria, has his PhD in physics and has been with the company for 13 years. After his studies at

the University of Würzburg, he joined the applications laboratory at NETZSCH-Gerätebau and became head of the same only a few years later. In July 2007, he was promoted to "Head of Applications & Services".

Dr. Thomas Denner, who has been Managing Director of NETZSCH-Gerätebau GmbH responsible for "Technology & Administration" as well as Division Manager for the Analyzing & Testing business unit since September 1st, 2005, will find a strong personality at his side in Dr. Jürgen Blumm.

We wish Dr. Jürgen Blumm much success in his new position.

Analysis of the Composition of the Cuticula (Shell) of Isopods

Dr. Frank Neues, Prof. Matthias Epple
Institute for Inorganic Chemistry, University of Duisburg-Essen

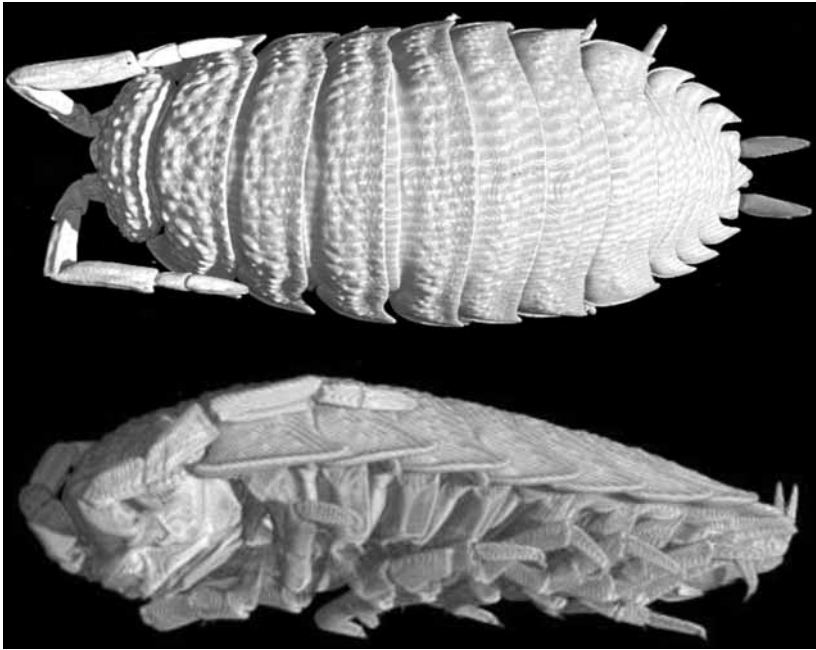


Fig. 1. Overview of *P. scaber* using SR μ -CT, top view (upper) and transversal from the side (lower). Only the mineralized parts (cuticula) of the animal are imaged because these have higher X-ray absorption.

The term "Isopoda" (woodlice and related species) describes an order of animals belonging to the Malacostraca class. The next higher classifications are the subphylum Crustacea and phylum Arthropoda, to which 80 % of all animal life forms belong, including insects, spiders, scorpions and millipedes. Arthropods live in almost all habitats, spanning from the poles to deserts, from the highest mountains to the deepest seas, and even underground or inside of other living creatures.

They first evolved in the Cambrian Period more than 500 million years ago. Over the course of time, a great variety of them have evolved, and some – like the trilobites – are also already extinct. Fossil records suggest that the Euthycarcinoid group of arthropods were the first terrestrial creatures.^[1] 75 % of all Crustaceans

are classified in the Malacostraca class. In addition to isopods, this class also counts crabs, lobsters and crawfish among its members. 3600 spe-

cies of isopods are terrestrial and 5400 are aquatic.^[2]

Figure 1 shows an image of the isopod *Porcellio scaber* taken using synchrotron radiation-based micro computer tomography (SR μ CT). The image shows only the mineralized parts of the body. These have higher X-ray absorption than the soft tissue and can therefore be shown separately. In contrast to vertebrates, isopods have an exoskeleton, i.e. no internal bones (endoskeleton), but only a mineralized shell. That is why isopods play such an important role as a model organism in biomineralization; they build up minerals in their exoskeleton (also called the "cuticula").^[3-5] The mineral portion consists of magnesium calcite, amorphous calcium carbonate (ACC)^[6,7] and amorphous calcium phosphate (ACP). A part of the isopods' magnesium substitutes the calcium in the calcite; it is therefore magnesium calcite.^[4] It is also presumed that the magnesium contributes to the kinetic stabilization

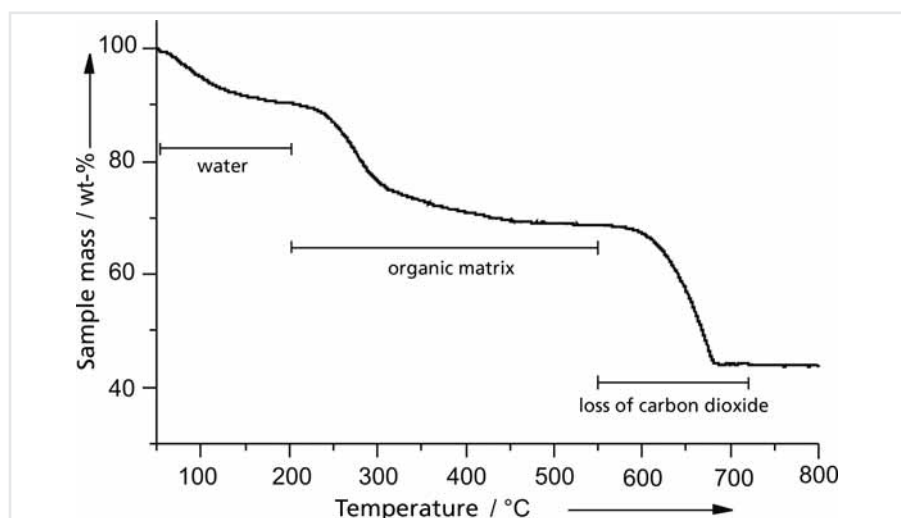


Fig. 2. Mass loss of the cuticula of *Philoscia muscorum*

Species	Ca	Mg	Water	Organic matrix	Entire mineral	CaCO ₃	Mg-calcite	ACC
<i>Philoscia muscorum</i> ^[13]	25.4	0.49	10.5	21.2	68.3	56.0	17.5	38.5
<i>Porcellio scaber</i> ^[4]	24.3	0.71	8.0	24.8	67.2	49.6	14.5	35.0
<i>Armadillidium vulgare</i> ^[4]	29.8	0.72	9.7	11.7	78.6	64.8	10.8	54.0
Species	ACC/ calcit w:w	Mg/Ca w:w	MgCO ₃ in Mg-calcit [mol%]	Mg in Mg-calcit	Mg not in Mg-calcit	Ca not in CaCO ₃	ACP	
<i>Philoscia muscorum</i> ^[13]	2.19	0.019	1.14	0.05	0.44	3.0	7.5	
<i>Porcellio scaber</i> ^[4]	2.41	0.029	3.63	0.13	0.58	4.5	11.2	

Tab. 1. Composition of the cuticula. Shown is the corresponding mass fraction w in weight-%, unless otherwise noted

(i.e. prevention of crystallization) of ACC.^[8-10]

The cuticulae of different kinds of isopods were analyzed by means of quantitative powder diffraction (XRD), thermogravimetry (TG) and atomic absorption spectroscopy

(AAS). Their compositions were then compared with the behavior and habitat of the respective creatures.^[4,13] The cuticulae of the animals were collected by Dr. A. Ziegler (University of Ulm).

Presented here is the analysis with

the example of *Philoscia muscorum*. Based on the powder diffractometric data, a Rietveld refinement was carried out which determined the proportion of crystalline magnesium calcite in the sample and the proportion of magnesium bound up in the Mg-calcite.

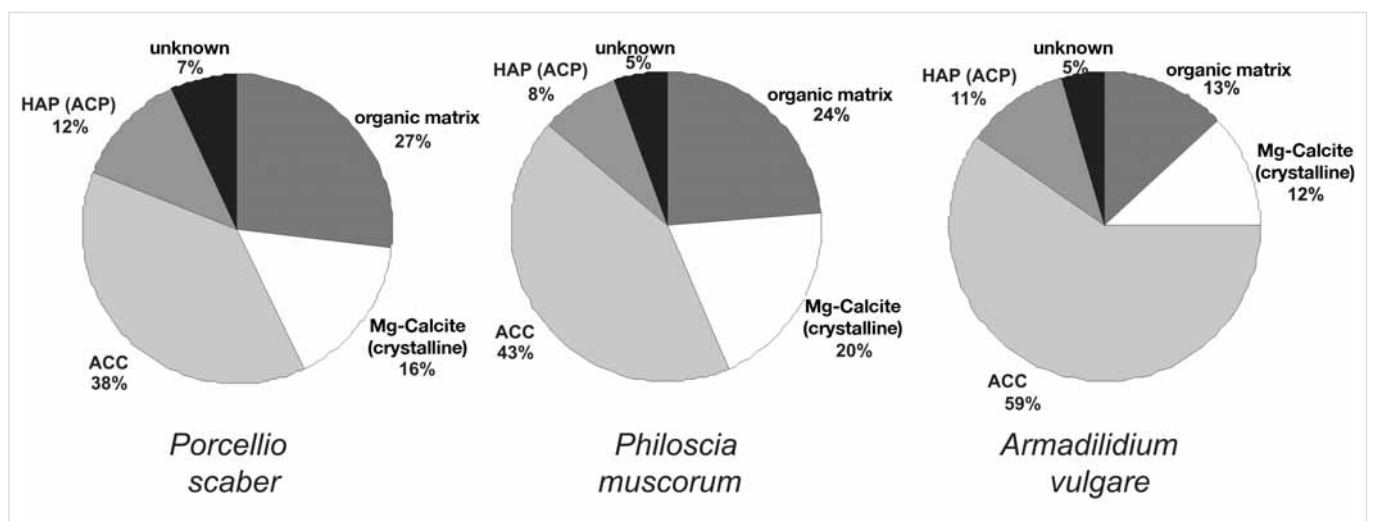


Fig. 3. Comparison of the cuticula composition of *Philoscia muscorum*, *Porcellio scaber* and *Armadillidium vulgare*

For the thermogravimetric analysis, the samples were heated at 3 K/min to 1000 °C in a dynamic oxygen atmosphere (figure 2). The evaporation of water (60 °C to 200 °C), the decomposition of the organic material (200 °C to 550 °C) and the decarboxylation of the carbonate (550 °C to 730 °C) can be seen.

During decomposition, mainly carbon dioxide and water are formed, and during decarboxylation, carbon dioxide. The resulting mass loss makes it possible to determine the amount of calcium carbonate in the sample. Since the amount of calcium carbonate is now known as a result of the thermogravimetric analysis, and the amount of magnesium calcite as a result of the quantitative powder diffraction, the amount of ACC can now also be determined.

Previous analyses have shown that not all of the calcium detected by means of AAS is bound up in the calcium carbonate.^[4] By analyzing the diffraction pattern of residuals of the thermogravimetric analysis (1000 °C), it was shown that the cuticula also contains amorphous calcium phosphate (ACP) which crystallizes during heating in the TG. The function of calcium phosphate in the cuticula is not yet known. *In vitro* experiments under physiological conditions have demonstrated that small amounts of phosphate prevent the crystallization of calcite.^[11,12] This may play a role in ACC formation and/or in improving the mechanical properties of the cuticula.

The results of the analysis are presented in table 1 and figure 3.

Additionally shown is the data for the species *Porcellio scaber* and

Armadillidium vulgare. It can be seen that the compositions of the cuticulae of *Philoscia muscorum*^[13] and *Porcellio scaber* are quite similar to each other. Both of these animals exhibit a similar tendency to flee from their natural enemies in self-protection. To be lighter and more flexible, their cuticulae are less mineralized than that of *Armadillidium vulgare*; this animal coils up in self-defense. Ten different kinds of isopods were analyzed and compared in the manner described.^[13]

We would like to express our thanks to Dr. Andreas Ziegler for the collection, preparation and dissection of the specimens.

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Prof. Matthias Epple



Dr. Frank Neues

The Authors

Prof. Matthias Epple studied chemistry at the Technical University of Braunschweig in Germany and received his PhD through Prof. H. K. Cammenga's study group on solid-state reactions and solid-solid phase transitions. He is now a professor of inorganic chemistry at the University of Duisburg-Essen, Germany.

Dr. Frank Neues studied chemistry at the University of Wuppertal, Germany. He received his PhD through Prof. Epple's study group at the University of Duisburg-Essen, focusing on the use of synchrotron radiation of bio minerals. He is currently a member of the scientific staff at the Jülich Research Center.

Characterization of Dust Samples in Occupational and Environmental Medicine

Dr. Dirk Walter

Institute and Out-Patient Clinic for Occupational and Social Medicine at the Justus-Liebig University, Giessen, Germany

Introduction

Nanotechnology is considered to be the key technology of the 21st century. It is expected that applications will be found not only in many areas of industry, but in new therapeutic and diagnostic procedures in the medical field as well. Nanoscale structures with dimensions entirely or partially smaller than 100 nm can actually generate new functionalities and properties. Such nanoparticles can be produced by means of the “bottom up” technique from gas and liquid phase reactions, or by means of the “top down” technique by the grinding or deforming of larger particles. Nanoparticles are also increasingly formed in modern combustion processes such as in diesel engines.

In view of these developments, it is urgent to clarify the health risks involved with nanoparticles and nanotubes (also called “ultrafine particles” in the occupational safety

field). Due to their small size, nanoparticles can easily be inhaled into the lungs and arrive all the way into the alveoli. Once deposited there, the particles can no longer be removed by the biomechanism responsible for cleaning the upper and middle respiratory tracts (“mucociliary clearance”) (figure 1).

If the particles deposited in the alveoli are “biostable” dust particles (i.e. they do not dissolve easily in the pulmonary liquid), then complex biochemical processes can take place which increase the potential for inflammation and even the risk of lung cancer. Penetration into the interstitium can also occur, thus allowing the nanoparticles to become systemically distributed.

An in-depth discussion about the potential hazards to human health of airborne biostable dust particles such as carbon black, modified carbon black, diesel exhaust particles

or toner material requires the use of state-of-the-art characterization methods. The reason for this is that concentration measurements carried out by particle counters (aerosol photometers), which until recently have been the primary tests conducted, have not been capable of explaining the different effects on the respiratory tract. Such measurement techniques do not allow any conclusions to be drawn regarding the size of the dust particles; in addition, the agglomeration behavior of the nanoparticles causes the biologically relevant concentrations yielded to be too low. Finally, such techniques provide no information on the chemical composition or particle surface.

Experimental work and results

A combination of electron microscopy and thermal analysis is best suited for characterization of the dust particles. Electron microscopy yields information on the morphology of the particles: dust agglomerates composed of primary particles 10-50 nm in size can be seen (figure 2). An elemental analysis (EDX) proved unsuccessful in identifying the dust for the primarily carbonaceous compounds.

Thermal analysis can be of further assistance here. TG-FTIR tests (TG 209 **F1 Iris**[®] with Bruker Tensor 27[™]) in an air atmosphere show differences in transformation behavior (decomposition and oxidation) at the same heating rate (20 K·min⁻¹). The FTIR coupling determines the composition of the gaseous oxidation products emitted (figure 3): Carbon black and modified carbon black oxidize in one reaction step into solely CO₂, whereas during oxidation of the

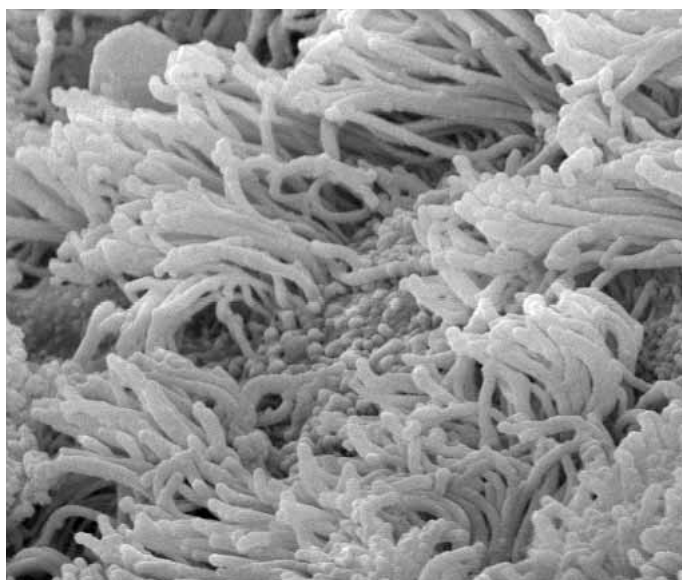


Fig. 1. Mucociliary clearance by cilia in the bronchiole wall; SEM micrograph, magnification 5000x

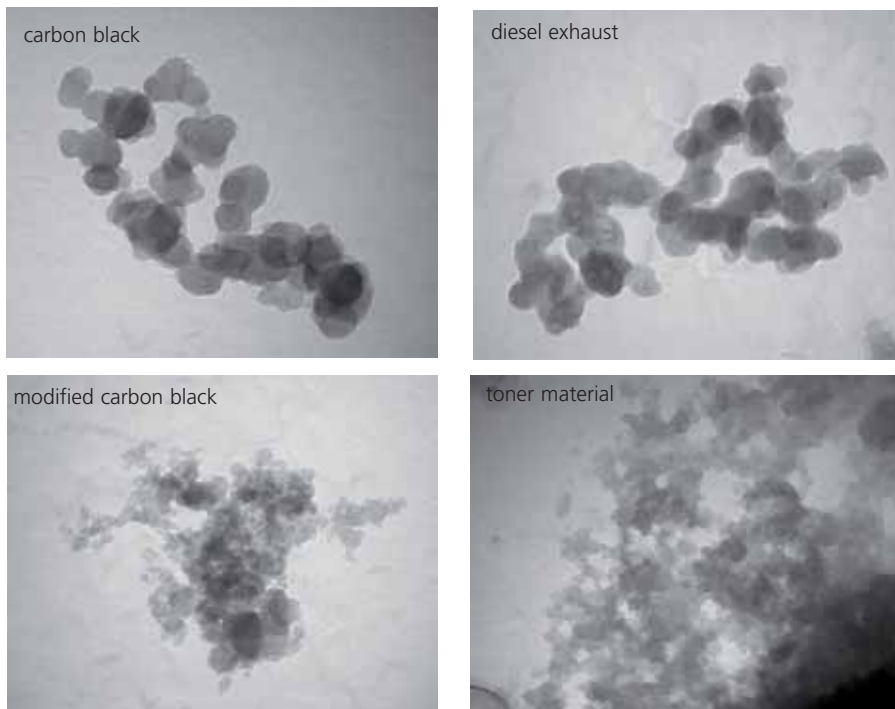


Fig. 2. TEM micrographs of the dust samples analyzed; magnification 100,000x

diesel exhaust particulates, CO₂ is developed in several steps and SO₂ is also produced (see figure 3). Toner initially generates aliphatic hydrocarbons, followed by CO₂ at higher temperatures.

Conclusion

Diesel exhaust particulates, carbon black and toner dust particles of interest in occupational and environmental medicine consist of agglom-

erates of toxicologically-relevant ultrafine particles which can barely be differentiated from one another, either optically under an electron microscope via particle size or morphology, or by means of elemental analysis. Due to their differing thermal stabilities, however, they can be differentiated quickly and reliably by means of thermoanalytical characterization. Even small amounts in the one-digit milligram range are sufficient, as they accumulate during dust measurements in the form of filter admission. The thermoanalytical results therefore allow for evaluation of airborne nanoscale dust in the fields of occupational and environmental medicine, and help in determining any necessary preventive measures to be taken in the interest of health protection.

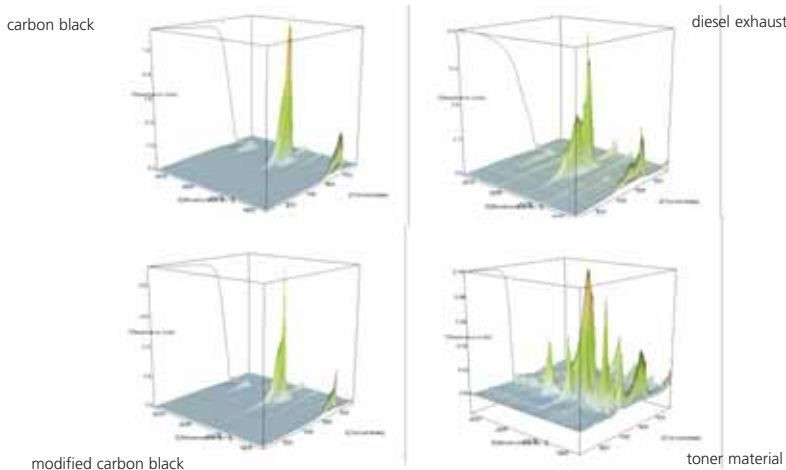


Fig. 3: Results of the TG measurements with subsequent FTIR analysis



The Author

Dr. Dirk Walter holds doctorate degrees in both the natural sciences and human biology. In 2006, he achieved his qualification to professorship in Inorganic and Analytical Chemistry at the Technical University of Berlin. Since 2007 he has headed the Hazardous Materials Laboratories for Chemistry and Physics at the Institute and Out-Patient Clinic for Occupational and Social Medicine of the Justus-Liebig University in Giessen, Germany.

Quantification of Decomposition Gases by Means of *PulseTA*[®]

Dr. Yu Hui-Mei, Analysis & Testing Center for Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences



Fig. 1. NETZSCH instruments at the Analysis & Testing Center for Inorganic Materials, Shanghai

In the field of building materials, more and more products being brought to market promote a self-cleaning, anti-fogging or anti-microbial surface. Responsible for these properties is the photocatalytic effect of nanoparticles of semiconductor metal oxides which are applied in thin transparent layers.

A photocatalytically active substance is characterized by the fact that when it is supplied with energy, e.g. by absorption of light, electrons from the valence band of the semiconductor are lifted into the conduction band. "Holes" thereby remain in the valence band and act as positive charge carriers. The electron/hole pairs can then react on the surface. This is an important condition for the creation of radicals, which also contribute to the decomposition of organic impurities.

For this purpose, pure or modified titanium oxide (TiO₂) is often used.

Traditionally, TiO₂ is used as a white pigment in paints, varnishes and polymers. It is chemically very stable, non-toxic and inexpensive. In nature, it occurs in three forms: as rutile (the form most thermo-dynamically stable in the solid state), as anatase and as brookite. Of the three, anatase has the highest photocatalytic activity.

After exposure to light, titanium oxide has an especially high affinity for water (photoinduced hydrophilia). The water drops simply spread into a paper-thin film, loosen any dirt particles and rinse them away. Such types of surfaces cannot fog up.

Activation of TiO₂ requires ultraviolet light with a wavelength less than or equal to 385 nm. Only 2 - 3 % of sunlight is in this wavelength range; the percentage for indoor artificial light is far less. This is the reason that the Analysis and Test Center for Inorganic Materials of the Shanghai

Institute for Ceramics at the Chinese Academy of Science has been working for years on alternative systems which can also be activated by means of visible light.

To this end, TiO₂/In₂O₃ was treated with ammonia at 580 °C for 8 hours in order to extract TiO₂/InN (In/(Ti + In) = 6.5:100 mol). X-ray diffraction (XRD) detected only titanium oxide since the highly disperse indium nitride clusters on the surface of the titanium oxide nanocrystals were not crystalline. It is therefore not possible to detect indium nitride by means of X-ray diffraction.

It is, however, possible by combining thermogravimetry, differential scanning calorimetry and mass spectrometry (TG-DSC-MS) with *PulseTA*[®].

For this purpose, the mass changes and gases released during thermal decomposition were analyzed on both pure InN and the nitrated TiO₂/In₂O₃ sample. It was shown that InN undergoes a single-step decomposition into indium and N₂ (figure 2) in an argon atmosphere between 550 °C and 750 °C. The determined mass decrease is equivalent to the stoichiometric value of 10.9 %. The release of gaseous nitrogen can be tracked with the help of mass spectrometry (N₂⁺, m/z = 28). The result is shown in figure 2 (upper part) as a function of temperature.

In case of the nitrated TiO₂/In₂O₃ sample, the corresponding mass change (TG) and release of nitrogen (N₂⁺, m/z = 28) were detected (figure 3) in the same temperature range. This is a clear indication that the indium nitride (InN) was synthesized by means of the reaction described above (ammonolysis).

Leading Thermal Analysis.

Since the TG curve in the TiO_2/InN measurement shows a continuous mass loss over the entire temperature range, the indium nitride could only be quantified with the help of the *PulseTA*[®] box. It enables quantification of the amounts of gas released, by injecting several gas pulses with defined volumes (in this case, N_2 pulses with volumes of 500 μl each) and then correlating the peak areas ($m/z = 28$) of the calibration peaks with the peak area of the decomposition reaction.

It can be concluded from the results that the combination of TG-DSC-MS and *PulseTA*[®] is very well suited for the characterization and quantification of the nitridation product.

More information on the experiments described can be found in:

- (1) Hui-Mei Yu et al., Thermal kinetic analysis on InN by TG-MS combined with *PulseTA*, *Thermochimica Acta*, accepted on July 23, 2006.
- (2) Yu Hui-Mei et al., Thermal behaviour of the nitrided $\text{TiO}_2/\text{In}_2\text{O}_3$ by TG-DSC-MS combined with *PulseTA*, *Thermochimica Acta* 440, 2006, pages 195 – 199.



The Author:

Dr. Yu Hui-Mei has been employed at the Analysis & Testing Center for Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences since 2002. Her current field of research focuses on the application of powerful methods for high-tech materials. She has been working with NETZSCH equipment for thermal analysis needs (STA 449 C *Jupiter*[®] TG-DSC, coupled to the Balzers Thermostar quadrupole mass spectrometer, see fig. 1).

We thank Dr. Yu Hui-Mei for providing us with this article.

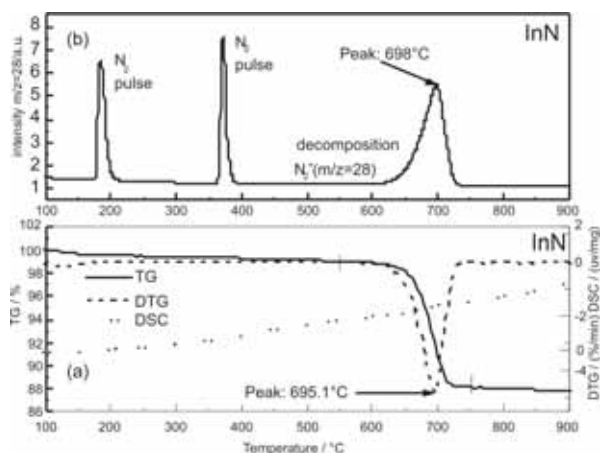


Fig 2. Thermal behavior of indium nitride, TG curve (bottom) and quantification of the release of nitrogen in the MS (top)

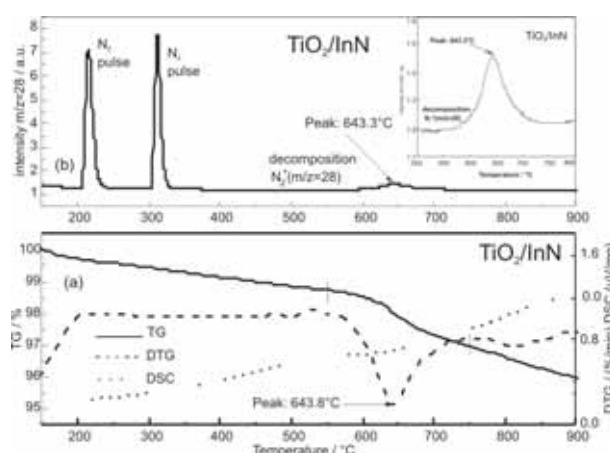


Fig. 3. Thermal decomposition of TiO_2/InN , TG curve (bottom) and intensity course of $m/z=28$ (nitrogen) together with two N_2 calibration gas pulses (top)

Component Kinetics

– an Excellent Tool for the Description of Reactions in Homogeneous Mixed Phases

Dr. Ekkehard Füglein, Dr. Elena Moukhina, NETZSCH-Gerätebau GmbH

With *Component Kinetics*, a new member has been introduced into the *Advanced Software* family, a set of supplementary programs to the NETZSCH measuring and evaluation software.

For more than 15 years, *Thermokinetics*, a formal kinetic approach, has been an essential part of these software enhancements and is employed intensively by many users, particularly in research, development and production control.

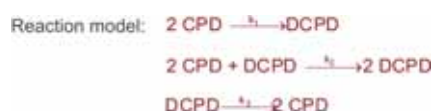
The objective of kinetic evaluation is to describe the measuring data as precisely as possible using a mathematical model. To accomplish this, a calculated model is varied until it is finally in agreement with the experimental data. When a suitable model is found, it can be used to optimize measuring times or to make predictions for conditions which would either be impossible or very time-consuming to measure.

Component Kinetics builds upon *Thermokinetics* and complements it by supplying additional possibilities. For example, the reaction steps can be entered as chemical reaction equations and can be freely formulated with regard to the reaction model. Different initial concentrations of reactants can be taken into consideration in the type and quantity of the solvents, catalysts or inhibitors.

This can be illustrated with the example of dimerization of cyclopentadiene (C_5H_6):

Dimerization of cyclopentadiene is an example of a [4+2] cycloaddition. The German chemists Otto Diels and Kurt Alder were awarded the Nobel Prize in 1950 for clarifying this reac-

tion type. Since then, this cycloaddition has been known as the Diels-Alder reaction. In the case of the dimerization of cyclopentadiene, it can be described as a combination of several single steps:



CPD: Cyclopentadiene, DCPD: Dicyclopentadiene

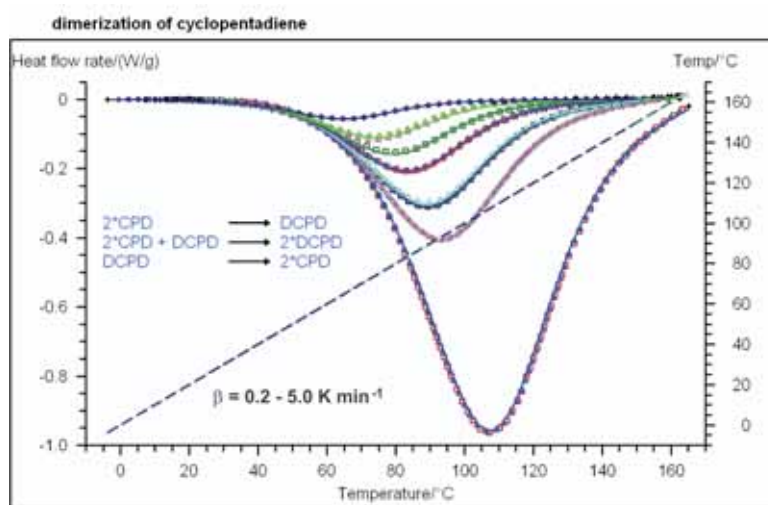
The partial steps can be entered in the program as a chemical reaction equation:

Reaktion	Reaktant	Produkt	Stoichiometrie	Einheit	Phase
1	2 CPD	1 DCPD	1	g	II
2	2 CPD + 1 DCPD	2 DCPD	2	g	II
3	1 DCPD	2 CPD	2	g	II

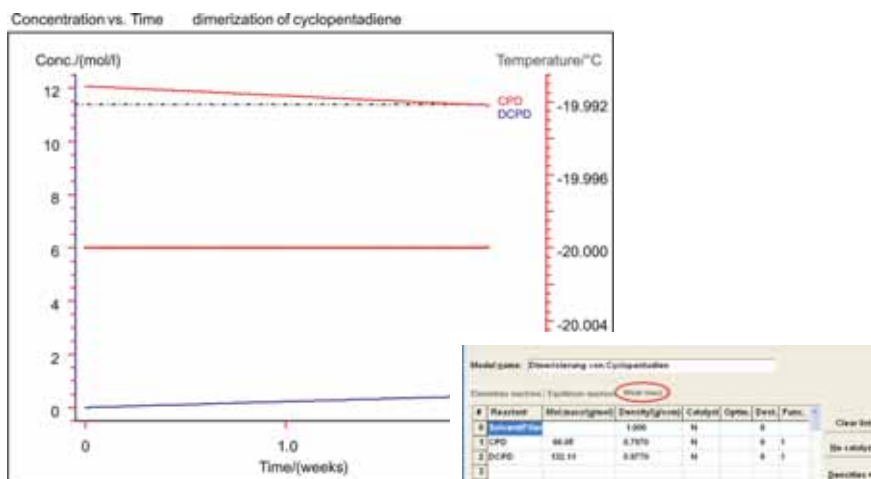
The density of the corresponding reactants can also be taken into consideration, as can their catalytic effect, among other things.

Reaktion	Reaktant	Produkt	Stoichiometrie	Einheit	Phase
1	2 CPD	1 DCPD	1	g	II
2	2 CPD + 1 DCPD	2 DCPD	2	g	II
3	1 DCPD	2 CPD	2	g	II

When fitted successfully, a comparison of the measurement data (symbols) with the calculated data (solid lines) shows a perfect description of the total reaction for different heating rates.



The handling of cyclopentadiene is difficult since - although it is obtained from the dimers by distillation at 150 °C to 170 °C - it dimerizes again considerably when stored at room temperature. The prediction of storage stability is therefore an important aspect which can be determined for each storage temperature with the help of *Component Kinetics*. For a storage temperature of -20 °C, our example yields a monomer loss of 0.42 % per day.



The Benchmark in High-Temperature DSC: The New DSC 404 *Pegasus*®

Dr. Alexander Schindler, NETZSCH Applications Laboratory, and Dr. Jürgen Blumm



Fig. 1. The new DSC 404 **F1** *Pegasus*® with automatic sample changer (ASC) for up to 20 samples

Along with the STA 449 *Jupiter*® (see title, page 1) NETZSCH is pleased to introduce the new DSC 404 *Pegasus*®. DSC stands for Differential Scanning Calorimetry and is one of the most efficient and therefore most widely used methods in Thermal Analysis.

With the help of DSC, nearly any energetic effect occurring in a solid or liquid can be analyzed. Melting, crystallization, (magnetic) phase transitions, glass transitions, and oxidative stability can be dealt with reliably, as can many other tasks, such as the determination of specific heat.

The new NETZSCH DSC 404 *Pegasus*® sets the benchmark!

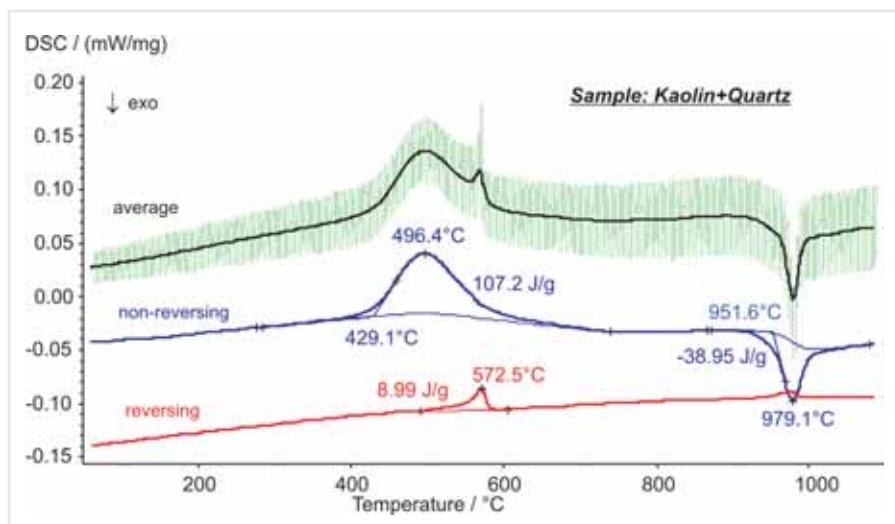


Fig. 2. Temperature-modulated DSC measurement on a kaolin quartz mixture (signal average value, non-reversing and reversing parts), measured with the DSC 404 **F1** Pegasus®

Many applications from fields such as ceramics, metals, plastics, and composites can be handled by the DSC 404 Pegasus® with high precision over an extremely broad temperature range (-150 °C - 2000 °C).

Built-in performance: the proven vertical and vacuum-tight construction not only make the DSC 404 Pegasus® easy to operate and robust, but also allow for measurements under pure gas atmospheres, which is especially important for samples sensitive to oxygen. The various DSC sensors feature optimal sensitivity, short time constants and excellent reproducibility.

Versatile possibilities for upgrading make the DSC 404 Pegasus® extremely flexible and powerful – now and in the future. The optional temperature-modulated DSC (TM-DSC) for the separation of reversing and non-reversing energetic effects is a unique feature in the field of high-temperature DSC (not available in North America and Japan). TM-DSC

is often employed in low-temperature applications, e.g. for polymers.

Figure 2 shows the measurement results for a kaolin quartz mixture. The irreversible dehydration and the phase transitions of kaolin were detected in the non-reversing part of the DSC signal at 496 °C and 979 °C (peak temperatures). The reversible

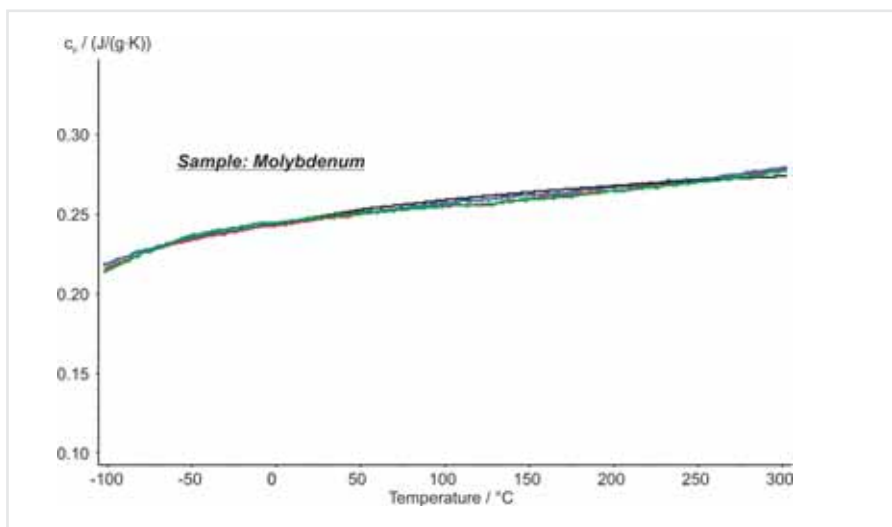


Fig. 3. Specific heat of molybdenum, measured three times with the DSC 404 **F1** Pegasus® (red, blue and green curves) along with literature values (black curve)

quartz transition occurred at 573 °C in the reversing part of the DSC curve.

The specific heat of molybdenum was measured three times between -100 °C and 300 °C with the new low-temperature furnace of the DSC 404 Pegasus®. Additionally depicted are the literature values for pure molybdenum (black line) between room temperature and 300 °C. The differences between the measured results and the literature values are generally less than 2 %. Also the reproducibility is better than 2 %.

This confirms the excellent performance of the DSC 404 Pegasus® for measurements of specific heat – even in the low-temperature range!

Our Events	Date	Location
2. Bondexpo - Trade Fair for Industrial Bonding and Technology	Sept 22 - 25	Stuttgart, Germany
Seminar: Rheology and Thermal Analysis	Sept 23 - 24	Nuremberg, Germany
analytica China 2008	Sept 23 - 25	Shanghai, China
GDCh Conference on Solid-State Chemistry & Material Research	Sept 24 - 26	Bayreuth, Germany
Tecnargilla 2008	Sept 30 - Oct 4	Rimini, Italy
testXpo - 17. Int. Forum for Materials Testing at Zwick	Oct 13 - 16	Ulm-Eisingen, Germany
FAKUMA - 19. Int. Trade Fair for Plastics Processing	Oct 14 - 18	Friedrichshafen, Germany
Expoquimica 2008	Oct 20 - 24	Barcelona, Spain
5 th International Thermoset Conference	Nov 20 - 21	Iserlohn, Germany

NETZSCH GEFTA Award 2008 to Erwin Kaisersberger



left to right.: Dr. Thomas Denner, Award-Winner Erwin Kaisersberger, Dr. Michael Feist

The annual convention of the National Societies for Thermal Analysis and Calorimetry from Germany (GEFTA), France (AFCAT)

and Switzerland (STK), which took place from June 18th through 20th, 2008, in Mulhouse, France, was a fitting occasion for the presentation of the NETZSCH GEFTA Award 2008 to physicist Erwin Kaisersberger. The award was presented by the GEFTA chairman, Dr. Michael Feist, in honor of Mr. Kaisersberger's 35 years of excellent scientific and applicational work in the field of thermal analysis and calorimetry.

Erwin Kaisersberger's scientific and technical expertise, along with his numerous publications and lectures

in high-temperature applications, polymers and pharmaceuticals, have made him to a world-renowned specialist. He entered his well-deserved retirement in the fall of 2007 but continues to work as a consultant for NETZSCH.

We congratulate Erwin Kaisersberger on obtaining the NETZSCH GEFTA Award 2008 and wish him and his family good health and all the best for the future.

Stephan Knappe
Head Application & Services

Imprint

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