ONset

NETZSCH
CUSTOMER MAGAZINE
Edition 25 | December 2022

More Rheology – Less Effort

When Super Strength Meets Shear Flexibility

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Editorial

Dear Reader:

At a time when we are facing ever-rising prices for energy and raw materials along with the consequent impact on production costs, we have to be creative to overcome such difficulties. We try to be aware of what is new, expand our knowledge and be constantly open to innovation.

This issue of **on**set features a variety of articles showing how thermal analysis and rheology can be applied in optimizing available resources and processes as well as finding new alternatives to these.

Our cover story about the Rosand high-pressure capillary rheometer describes how rheology is closely linked to process optimization. This rheometer characterizes the shear viscosity of materials under extremely high shear rates, and can also generate valuable data for flow simulation. The pVT analysis of HDPE (high-density polyethylene) serves as an example for this simulation model.

"DSC in Recycling" discusses the use of temperature-modulated DSC combined with *PeakSeparation*, a feature of our *Proteus*® software, and the *Identify* database within the field of plastics recycling. This application example elegantly shows the use of DSC for the identification and quantification of different olefins in plastic mixtures.
Find out more on page 8.

Under the *CUSTOMERS FOR CUSTOMERS* section, you can find the interesting article by Dr. Tim Gestrich and Dr. Mathias Herrmann from Fraunhofer IKTS, Dresden, focusing on future applications; the research group broadens its understanding of thermal processes and answers questions related to energy efficiency, CO_2 reduction, and resource conservation.

We Test It For You! We would like to share with you all of our experience in thermal analysis, rheology and fire testing by means of our wide portfolio of contract testing services; take a closer look on page 16.

Starting on page 18, the article under *PRECISE PRACTICE* demonstrates how the STA 449 ***F3*** *Jupiter*®, equipped with a humidity generator, can be used to mimic daily situations where environmental humidity affects matter. This illustrative example compares cloth and medical FFP2 masks exposed to moist respiratory air.

CUSTOMERS FOR CUSTOMERS: With their article, Dr. Dmitry Sergeev and Dr. Michael Müller from Forschungszentrum Jülich GmbH, Germany, describe the use of thermal analysis for generating experimental data that is used for the evaluation and screening of salt systems as high-temperature storage materials. More on this cutting-edge topic on page 20.

In this edition, we also highlight the launch of a new product: The VAB300x external valve box, an intelligent solution for the coupling of GC-MS to thermobalances.

Please don't miss the chance to look at our events, and much more. And last but not least, I proudly draw your attention to the 60th anniversary of NETZSCH- Gerätebau GmbH, which we have been celebrating throughout the year.

I hope you'll enjoy your browse through our **on**set 25!

Souza

Yours truly,
Dr. Ligia Elena de Souza
Business Field for Pharmacy, Cosmetics & Foods

Process Optimization by Rheology

Dr. Levente Szántó, Project Leader Technology and Rheology Product Management

Introduction

Nowadays, steadily growing energy prices for gas and electricity result in highly expensive polymeric raw materials and rising processing costs. Therefore, resource-, cost-, energy- and eco-efficiency is more important than ever. The aforementioned objectives cannot be achieved if the effectiveness of the manufacturing processes is not (re)considered, i.e., if the process is not optimized and tailored to the processed polymeric material or vice versa. Process optimization needs to start with understanding the flow behavior of the polymer employed. That's where rheology comes into play.

Rheology is the study of the deformation and flow of matter, unveiling the flow behavior of complex fluids such as polymers, food, slurries, suspensions and other compounds [1]. Rheometers such as rotational and/or high-pressure capillary rheometers contribute to better understanding the rheological properties of the materials being analyzed (Figure 1). However, in order to optimize the processing conditions, the materials must be investigated at comparably high shear rates and temperatures. Nevertheless, flow simulations may also substantially contribute to better manufacturing efficiency. Therefore, along with the rheological properties, also the parameters relevant to flow simulation shall be determined.

The Rosand high-pressure capillary rheometer line (Figure 2) allows for examination of the materials at process-relevant shear rate ranges up to extremely high shear rates (~10^8 s^{-1}). Besides the shear dependency of the viscosity (shear thinning, shear thickening, Newtonian behavior), the rheological behavior under extensional flow can also be

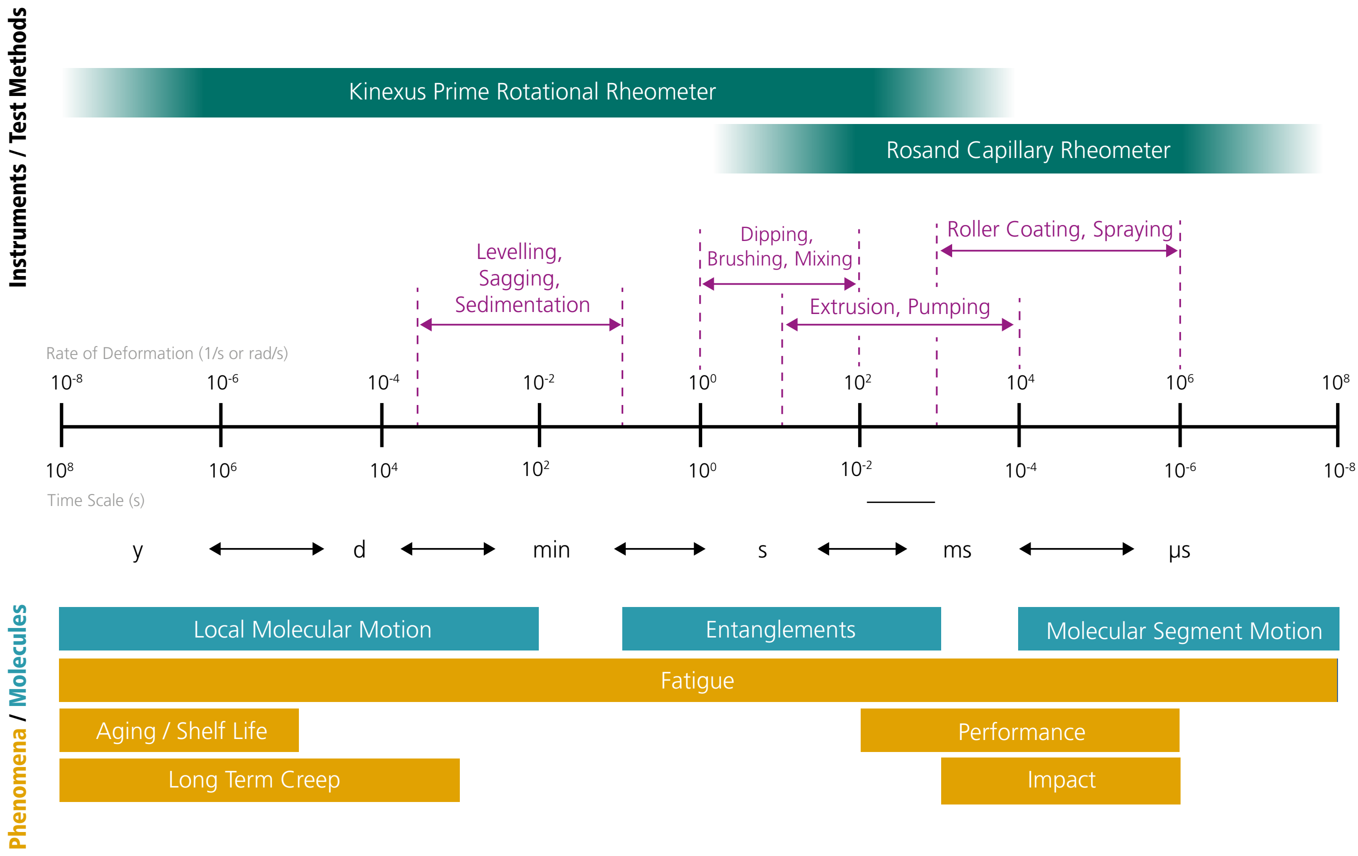

Fig. 1. Shear rate range covered by our rotational and capillary rheometers and its relevance in processing and understanding molecular dynamics

Rosand Capillary Rheometer

Shear thinning is a phenomenon occurring with some non-Newtonian fluids in which the fluid viscosity decreases with increasing shear stress.

Shear thickening is the opposite phenomenon.

In contrast with both of these, the viscosity of a **Newtonian fluid** is independent of the applied force (shear stress).

See for more definitions:
https://analyzing-testing.netzsch.com/en/training-know-how/glossary

analyzed. Moreover, by means of pVT measurements, simulation-relevant parameters such as pressure-dependent specific volume, crystallization or melting temperature are accessible as well.

In simple terms, the working principle of a high-pressure capillary rheometer for determining the shear viscosity of a material is that the material (molten polymer, liquid, paste, food, cream, etc.) be pressed with a well-controlled piston speed from a barrel through a capillary (die) with a well-defined diameter, length and entrance angle. The precise characteristics of the die, barrel and piston speed are necessary to later establish the shear stress (σ_{app}, see *Eq. 1*) and shear rate ($\dot{\gamma}_{app}$, see *Eq. 2*). Thus, the viscosity of the processed sample can be determined (η_{app}, see *Eq. 3*) [2].

$$\sigma_{app} = \frac{PR}{2L} \qquad (1)$$

$$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3} \qquad (2)$$

$$\eta_{app} = \frac{\sigma_{app}}{\dot{\gamma}_{app}} \qquad (3)$$

Where P is the pressure, R and L are the radius and length of the die, respectively, and Q is the volume flow rate.

Fig.2. Rosand RH7/10 Capillary Rheometer

pVT Measurement

In order to fully exploit the capabilities of a Rosand high-pressure capillary rheometer and contribute, by means of the data obtained, to process optimization, measurements must also be carried out along with shear and/or extensional measurements. In contrast with such shear and extensional measurements, the sample during a pVT measurement is enclosed in the barrel and the die is closed. This is necessary for investigating the change in sample volume as a function of pressure. Furthermore, first-order transitions can also be detected. The information obtained can be used in process simulation together with the shear viscosity measurement.

Rosand Capillary Rheometer

HDPE Under Pressure – Process Optimization

In the following, a Rosand RH7/10 high-pressure capillary rheometer with a maximum force of 100 kN was employed to unveil the pVT behavior of a high-density polyethylene (HDPE). The measurement was performed under isothermal conditions in the temperature range between 190°C and 40°C (cooled in steps of 10°C). The pressure range varied from 1 MPa (10 bar) up to 100 MPa (1000 bar). To increase the efficiency (less material and shorter measurement time), the Low-Level Script software option was used. Thus, multiple isotherm analysis sequences were created. For the duration of the experiment, in order to avoid any leakage, a PTFE seal was mounted on the piston end tip. Care must be taken to ensure that no air bubbles are formed during sample preparation (filling and compacting). Their presence and the resulting incorrectly determined weight lead to errors that strongly influence the quality of the measurement. Hence, not only can information regarding the pressure-dependent volume change be gathered, but it is also possible to measure the specific volume, density, and crystallization and melting temperature.

Precisely controlled piston movement (speed) compresses the HDPE at the desired pressure. A high-accuracy pressure melt-transducer measures the pressure (see Figure 3).

Knowing the applied pressure, the actual position of the piston, and the exact weight of the sample, the specific volume is calculated. Using third-party software, it is possible to plot a 3-D diagram (pressure, specific volume, temperature in Figure 4). This conveys further understanding of the material behavior (crystallization temperature, density) under

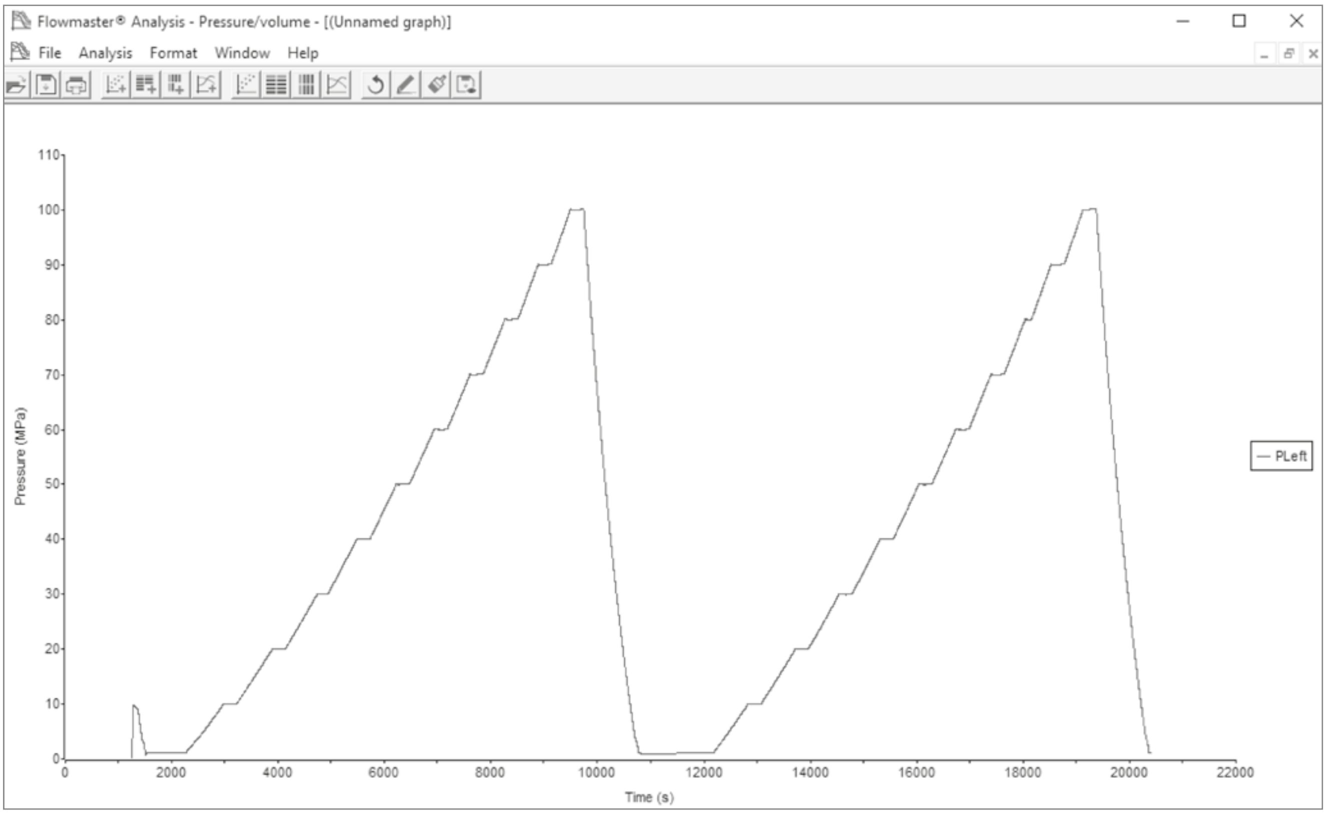

Fig. 3. Course of pressure as a function of time during a pVT measurement on HDPE

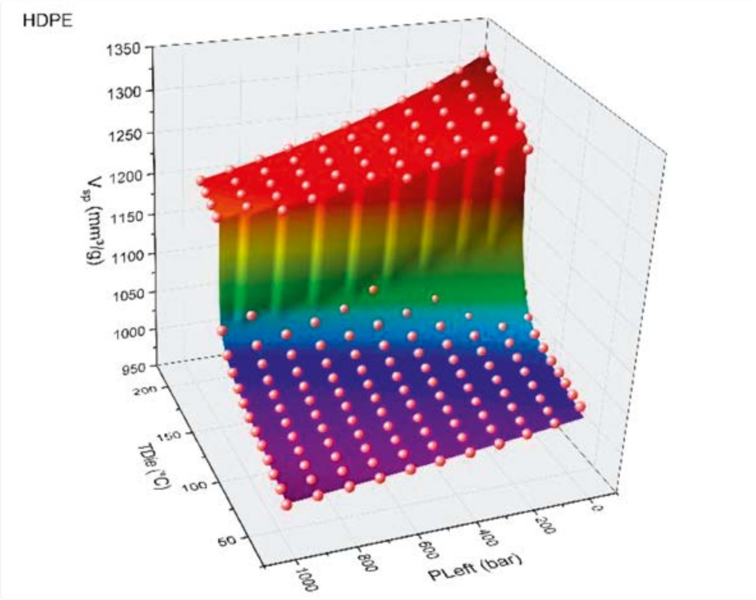

Fig. 4. Pressure-specific volume-temperature diagram of HDPE

high pressures and temperatures. Furthermore, processing-relevant parameters for flow simulation can be obtained by fitting the modified two-domain Tait [3] surface function to the data gathered from the pVT analysis. Later on, by combining the information originating from shear and pVT measurements, it is possible to significantly contribute to process optimization, thus achieving resource-, cost-, energy- and eco-efficiency objectives.

Summary

Investigation of the rheological properties of materials by means of a high-pressure capillary rheometer also allows, in addition to the determination of the shear rate dependence on the shear viscosity at extremely high shear rates (~10^8 s^{-1}), the determination of parameters relevant for processing and simulation. These parameters can be obtained, for example, by performing pVT measurements.

A Rosand high-pressure capillary rheometer offers insights toward better understanding of the material behavior. Such insights guide scientists in the creation of tailor-made, innovative materials and solutions. This later on significantly contributes toward optimizing industrial processes through increased efficiency and output, thus achieving multiple higher-tier objectives.

Literature

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DSC Analysis to Identify Recyclates

Dr. Omeir Khalid, International Sales, and Dr. Natalie Rudolph, Polymer Business Field Management

Introduction

Packaging applications make up around 50% of plastic production. Since plastics have poor biodegradability, but are a valuable resource even after their service life, focusing on recycling pathways is of utmost importance [1].

The majority of plastics used in packaging are polyolefins, namely PP and PE like HDPE, LDPE and LLDPE. Thus, a combination of these materials is found in our recycling streams. The most common identification tool, Fourier Transform Infrared Spectrometry (FT-IR), is easy to use and delivers fast results for the vast majority of plastics, but it cannot differentiate between the different polyolefins (PO) due to their similarity in chemical structures and bondings.

DSC for the Analysis of Compositions

Differential Scanning Calorimetry (DSC) has been proven to be suitable for the analysis of mixed plastic waste and recycled polyolefin blends [2-5]. The significantly different melting temperatures of the materials can be used to identify the various components of a mixture, while their weight percentage is estimated based on the measured melting peak areas. In many cases, the peak areas of PP and PE found in such mixtures overlap, which requires mathematical separation of those signals. For this purpose, a DSC study on mixtures of HDPE-PP in various proportions was carried out using DSC measurements, *PeakSeparation* analysis, and the *Identify* database in the *Proteus*® software.

In order to better define the analysis range of each overlapping peak, temperature-modulated DSC (TM-DSC) was used for refinement. All experimental parameters and further information can be found in Application Note 265.

Experimental

The experiments were carried out with a DSC 214 *Polyma* using *Concavus*® pans with sealed and pierced lids. Other DSC instruments like the DSC 300 *Caliris*® can be used just as well.

Conventional DSC experiments at a heating rate of 10 K/min were performed while the DSC signal of the 2nd dynamic heating segment was used for compositional analysis. The TM-DSC measurement mode is additionally employed to improve the analysis procedure.

In particular, the overlaying melting peaks of HDPE and PP were separated in this work with the help of the *PeakSeparation* function, and the peaks obtained thereby were compared with entries in the *Identify* database in order to determine the polymer components present in the specimen. Furthermore, the components were then quantified based on their generated melting peak areas; however, in order to obtain reasonable values for the melting peak areas (melting enthalpies) which result from the areas between the DSC curve and its corresponding baseline, the temperature range within which melting of the HDPE and PP components actually occurs must be set properly.

TM-DSC curves for melting effects comprise a contribution to both reversing and non-reversing DSC signals. Therefore, TM-DSC experiments were carried out on the pure HDPE and PP samples in order to reveal the temperature range in which melting truly takes place.

Measurement Results

HDPE

In Figure 1, the TM-DSC results for pure HDPE are shown. While the solid line represents the total DSC signal, the dotted and dashed lines reveal the reversing and non-reversing signal proportions, respectively. For HDPE, melting starts already at about 0°C, as can be seen from the emerging non-reversing signal at this temperature. In the case of PP (not shown), the non-reversing signal emerges at about 20°C to 30°C.

Based on these findings, the lower temperature limit for the melting range of the HDPE/PP polymer blends during the *PeakSeparation* step is defined as 30°C. Here, the non-reversing signal of HDPE (see Figure 1) exceeds 1% of its total integral value, revealing significant melting at this temperature.

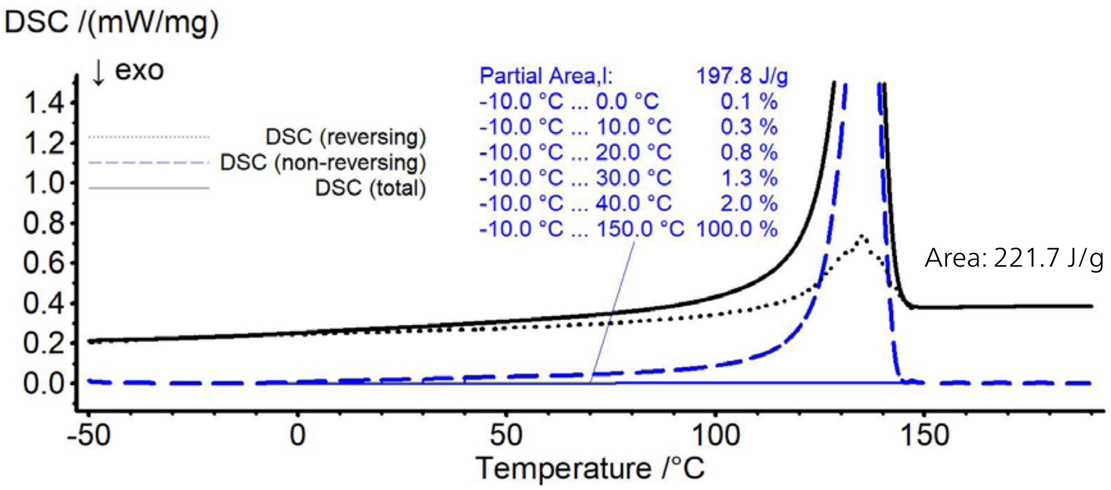

Fig. 1. TM-DSC result for pure HDPE showing the average DSC signal with a solid black line, the reversing signal portion with a dotted black line and the non-reversing signal portion with a dashed blue line.

HDPE Plus PP

In Figure 2, the DSC measurement of an HDPE/PP sample with 20% HDPE and 80% PP (PE20) is shown with a black solid curve. The *PeakSeparation* function is applied (30°C to 190°C, linear baseline, 2 peaks with asymmetric shape) to reveal the blue curve, which represents the HDPE component, and the green curve at higher temperatures, which represents the PP component. The red curve reflects the superimposition of both the blue and green curve as a fit function to the actual measured DSC signal (black curve).

At this point, the new mathematically generated peaks can be selected for comparison with entries in the *Identify* database, as shown in Figure 2 with the left blue peak. The database identifies the component as HDPE and presents the DSC curve of the HDPE database entry in pink for direct comparison. While here, the polymer blends are of known composition, the operator may then use these features to identify the individual components. This step is necessary for the following compositional analysis/quantification.

To quantify the HDPE and PP proportions in the PE20 sample, the peak area of HDPE calculated and shown in Figure 2 (44.0 J/g) needs to be divided by the specific melting enthalpy of the pure HDPE sample. That value can either be measured if the pure sample is available or can be taken from literature. However, literature values can vary significantly due to their different crystallinity degree. The HDPE/PP blends were obtained by mixing the commercially available pure substances, though it was possible to measure the specific melting enthalpy of pure HDPE directly at a value of 221 J/g as shown in Figure 1. Thus, the calculated HDPE content in the PE20 sample amounts to 19.8% (44.0/221.7). The HDPE content for other proportions was determined as well and summarized in Table 1.

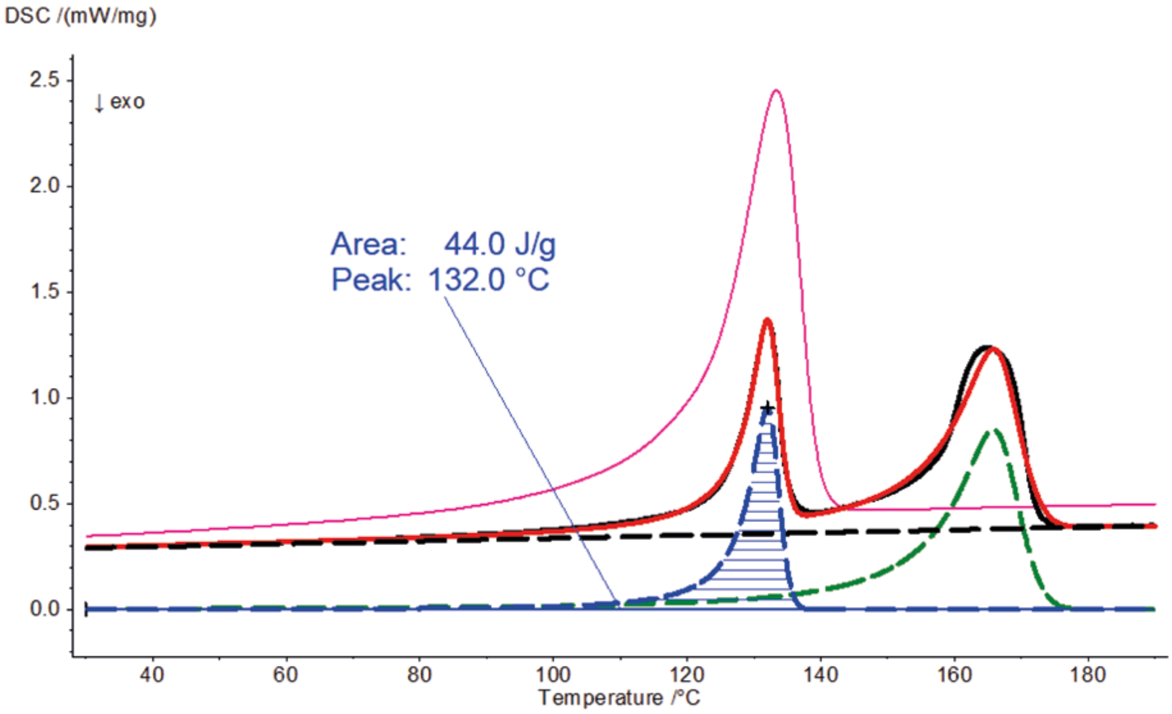

Fig. 2. Comparative presentation of the DSC result of sample PE20 (black solid line), the peaks generated by applying *PeakSeparation* for HDPE (blue dashed curve) and PP (green dashed curve), the cumulative curve of both separated peaks (red).

Table 1. HDPE content for other proportions

Sample	PE10	PE20	PE30	PE40	PE50	PE60	PE70	PE80	PE90
% PE actual	10.3	20.5	30.0	40.2	49.8	60.0	71.0	79.1	89.9
% PE calculated	9.7	19.8	29.2	39.4	49.3	57.3	70.5	79.5	88.0

For further details on the study, please refer to Application Note 266 → http://netzs.ch/AN266_EN

Conclusion

The calculated HDPE and PP portions obtained by *PeakSeparation* with two peaks, and the identification using the *Identify* database show very good agreement with the actual composition. TM-DSC is best known for distinguishing between simultaneously occurring reversing and non-reversing effects. However, in this example, temperature modulation is used to precisely reveal the onset of melting, which is sometimes difficult to determine visually due to the broad peaks with elongated shoulders towards lower temperatures that are often seen with polymers. Thereby, it was shown that TM-DSC provides a means of improving the prediction quality through refining of the analysis range.

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Analytical Compentence Far Beyond Ceramics Production

Dr. Tim Gestrich, Thermal Analysis and Thermophysics Group Leader, and Dr. rer. nat. Mathias Herrmann, Sintering and Characterization Department Head, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany

In Germany, nearly 70 percent of the energy used in industry is spent on thermal processes. Complex questions have to be answered, especially with regard to energy efficiency, CO_2 reduction and conservation of resources. These almost always involve interactions – for example, between temperature, time and gas atmosphere – and what influence they have on product properties and production processes. The "Thermal Analysis and Thermophysics" Work Group at Fraunhofer IKTS gets to the bottom of thermal processes.

Since its beginnings in the 70s, a lot has happened in the laboratories: Simple measurement instruments with analog data output for thermoanalytical and thermophysical parameters have been replaced by modern, digital equipment. In the course of digitalization, data is increasingly coupled and made usable for modeling thermal processes and component properties.

"There are two main pillars: Thermal analysis and characterization of thermal properties", explains Dr. Mathias Herrmann, Head of the "Sintering and Characterization" Department to which the work group belongs. On the one hand, researchers support the other departments at IKTS in their development efforts; on the other, they are available to industrial companies as providers of research and technology services.

First Main Pillar: Thermal Analysis

The field of thermal analysis (Figure 1) historically grew out of the development of ceramics and hard metal. "We are working with instruments which allow for defined thermal treatment with simultaneous measurement of the mass or length change or even energy flows. One of our specialties here is working under extreme conditions. By this we mean, for example, high or very low temperatures (-160°C to 2400°C) or very large or very small sample dimensions. This also includes high purity of the atmosphere, use of gas mixtures or doping, and measurements under explosive or hazardous atmospheres (hydrogen, carbon monoxide, hydrogen sulfide, etc.)," explains group leader Dr. Tim Gestrich. The researchers know exactly when gases form in the ceramic part caused by means of the mass change during heating. Then, the process temperature must be increased only slowly. Otherwise, the mold could be damaged by the expanding gas. This additionally saves energy, since the energy-intensive heating process can be precisely controlled. Further analyzers are available for characterizing the gases evolved. This way, the processes can be understood and optimized.

Fig. 1. View of the NETZSCH instruments in the laboratory at Fraunhofer IKTS (©Fraunhofer IKTS)

An example of the use of different analytical methods for elucidating the processes involved in the sintering of hard metal is illustrated in Figure 2.

The length change behavior due to sintering of the material is determined (with a NETZSCH DIL 402 ES/1). The detection of the reduction of surface-bond oxides by carbon from the mixture (at approx. 350°C, 750°C and 950°C) and the melting of the metallic binder phase (from approx. 1250°C) is detected by DSC measurements (NETZSCH DSC 404/1).

By means of thermogravimetric investigations, coupled to mass spectrometry (NETZSCH STA 429/3 and

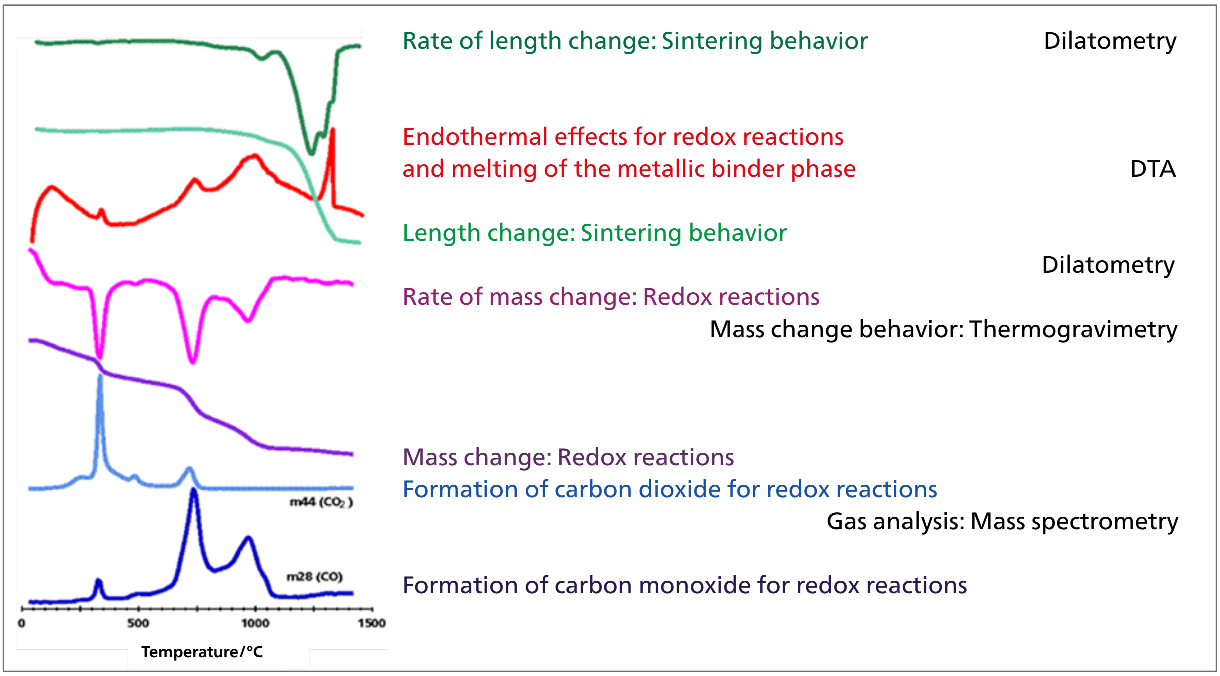


Fig. 2. "Complex“ thermal analysis of reactions during sintering of a superfine-grained hard metal (©Fraunhofer IKTS)

BALZERS quadrupole mass spectrometer QMG 422), the mass change behavior during these reactions can be analyzed. At lower temperatures, a higher proportion of carbon dioxide is detected and at higher temperatures, a higher proportion of carbon monoxide is detected. Furthermore, compared to the DSC measurement, additional outgassing or reduction effects can be observed at approx. 300°C (formation of carbon dioxide) and approx. 500°C (formation of carbon dioxide and carbon monoxide), which are associated with only minor caloric effects.

Figure 3 shows the analysis of the melting behavior of an additive for liquid phase sintering of SiC ceramics to very high temperatures (approx. 2000°C). The investigations were carried out with a well-maintained NETZSCH

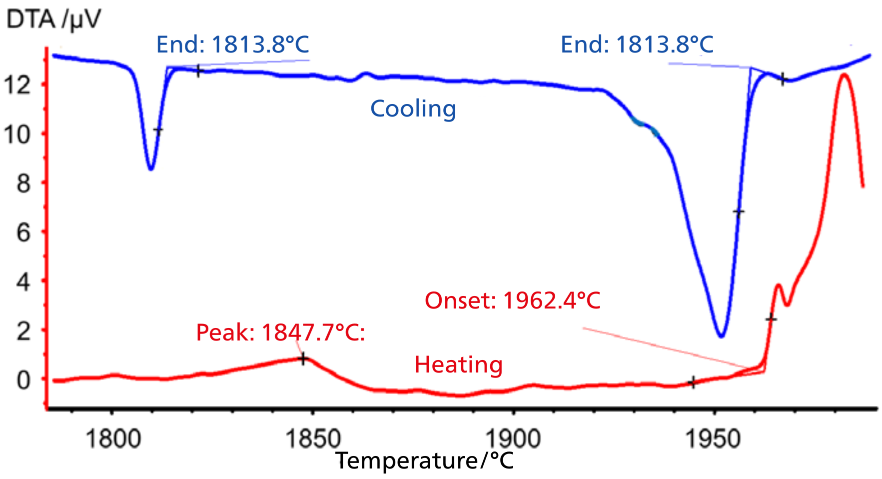


Fig. 3. Melting and solidification behavior of an AlN-Al_2O_3 sintering additive for the liquid phase sintering of SiC ceramics (©Fraunhofer IKTS)

STA 429 (built in 1977). During heating, endothermic reactions caused by the synthesis of the binder phase can be detected over a wide temperature range (approx. 1820°C to 1865°C). At approx. 1960°C, melting and further reactions or reactions accelerated by the liquid phase occur between the components of the initial mixture. During cooling, solidification of the binder phase also begins at approx. 1960°C. Beginning at approx. 1815°C, entire eutectic solidification of the binder phase occurs.

From Optimal Ceramic Firing Processes to CO_2-Free Raw Material Production

Precise analysis of thermal processes, however, is not only of interest for the production of ceramics or hard metals; it can also be transferred to other thermal processes, such as materials for batteries. Such data are also necessary for Industry 4.0 and the digital twin – without reliable material characteristics, thermal processes cannot be mapped.

Further examples are the production of metals and chemicals. The starting point is often oxygen-rich compounds such as ores, sulfates or minerals, which are thermally transformed into the desired raw material with the release of CO_2. If raw material production is to be successful in the future without CO_2 emissions, processes must be converted from fossil-reducing agents to hydrogen. In the best-case scenario, these processes only produce environmentally compatible water vapor. Since other temperature profiles are required for this, care must be taken to ensure that no undesirable side processes occur. Optimal final temperatures and reaction times are determined under laboratory conditions in order to implement such transformation processes in industry.

Second Main Pillar: Thermophysical Analysis

If components or machines such as turbines or engines are to be optimally designed, the thermophysical properties – such as thermal conductivity, specific heat capacity and the expansion coefficient – must be known. Fraunhofer IKTS holds DAkkS accreditation for these methods, ensuring the high quality of the data. The results then form the basis for the simulation of larger parts and furnace processes. The researchers' focus is basically on two different issues: The material behavior itself and the behavior of the part.

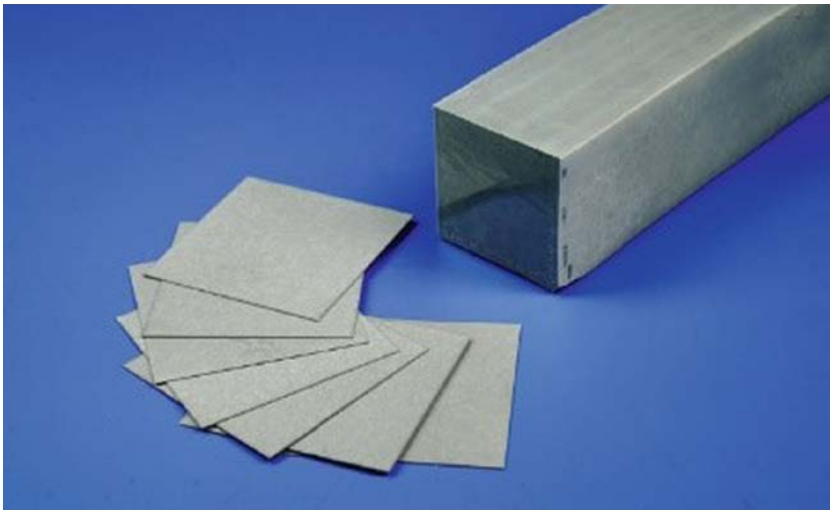


Fig. 4. Thermophysical analyses help reproducibly design manufacturing processes for new substrate materials in power electronics and significantly improve thermal conductivities (©Fraunhofer IKTS)

Improved Thermal Conductivities for New Substrate Materials in Power Electronics

Thermophysical properties also play a role in power electronics. Here, Tim Gestrich and his team are characterizing new substrate materials that quickly dissipate heat – for such applications as rectifiers and converters in cars, or solar- or windmill-powered plants (Figure 4). Raw materials such as silicon nitride substrates with thermal conductivities of more than 100 W/m·K are developed from low-cost raw materials. In another project, IKTS developed novel silicon-carbide-bonded diamond materials featuring thermal conductivities of over 600 W/m·K, i.e., 50% more than copper. While other diamond materials have to be manufactured under high pressure, the underlying processes of Fraunhofer IKTS do not require high pressures and thus, also do not require high energy input. In order to make such production processes more reproducible as well as to achieve excellent thermal conductivities, the know-how of the analytics group was also needed.

Vision for the Future

The “Thermal Analysis and Thermophysics” work group, currently comprising five employees, has worked with more than 500 companies to date and conducted nearly 70,000 experiments in the 30 years since the foundation of IKTS Dresden. In the long term, it is the researchers’ objective for the analytical competencies to take on increasing importance in the circular economy. The recycling of hard metals, in which critical raw materials such as tungsten and cobalt are recovered and reprocessed, is a well established procedure. The recycling of technical ceramics and battery materials (Figure 5), however, is still a high-potential area. To this end, the researchers at Fraunhofer IKTS are generating thermal and thermophysical data over the entire product life cycle to be able to derive new strategies for resource conservation. “We see our future in integrating our data into thermal modeling processes – which we can then use to model and understand manufacturing and recycling processes along with usage behavior and optimize them in terms of heat consumption and product quality,” says Mathias Herrmann.

Due to the strongly developing digitalization processes (Industry 4.0), parameters in the industrial process can increasingly be measured in real time and correlated with data from the laboratory. This way, effective time- and event-controlled profiles for thermal processes can be realized. The NETZSCH Kinetics Neo software package, among others, has proven worthwhile for this purpose.

Fig. 5. Data from the thermal and thermophysical analyses form the basis for thermal modeling processes that can be used to optimize recycling processes for batteries, among other things (©Fraunhofer IKTS)

We Test It for You!

Aileen Sammler, Content Marketing Manager

Along with a wide product range related to thermal analysis, rheology and fire testing, NETZSCH offers a service portfolio that includes application measurements and contract testing to help customers minimize risks, improve quality and save costs.

Application Measurements and Contract Testing With Precision

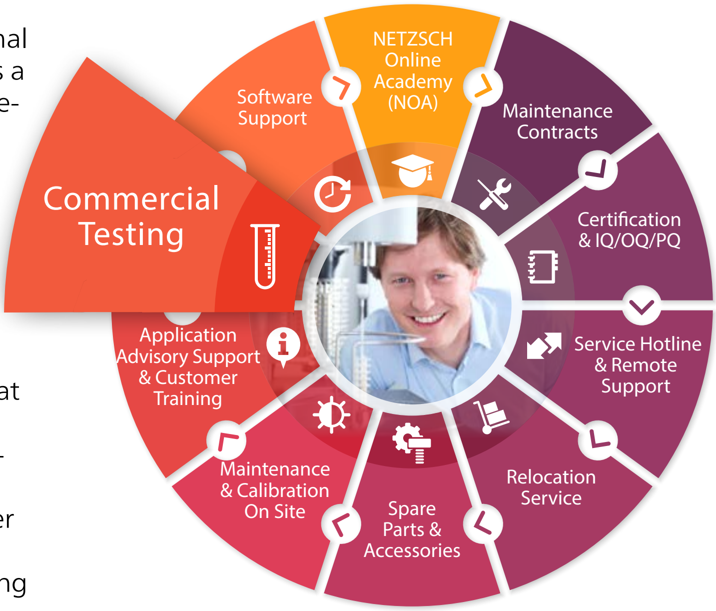
NETZSCH offers a variety of measuring methods that record information about mass changes, thermal stability, phase transformation temperatures, viscoelastic and rheological behavior, thermal diffusivity and thermal conductivity, length changes and other results (see Table 1). A temperature range from -180°C to 2800°C allows for flexibility while attaining accurate results for measurements under extreme conditions (e.g., high temperatures, vacuum, etc.). The techniques used further ensure that samples of different geometries and configurations (e.g., compact sample, powder, liquids) can be tested and analyzed. Our customers from a wide range of applications, such as automotive, plastics, electronics, chemical, air/space travel, pharmacy, food, cosmetics and ceramics have used our laboratory services for decades.

We offer contract testing in our application laboratories, for example, at our headquarters in Selb, or NETZSCH Instruments North America, LLC, Boston, USA.

Our Offerings

Our customer journey is tailored to the specific needs of each company and begins with sample preparation. The state-of-the-art approach and diverse measurement methods that are used at NETZSCH allow to answer specific and detailed questions and to deliver useful interpretations and recommendations going far beyond the purchase of an instrument.

During the entire process, customers are provided with expert knowledge from different academic specialities; chemists, physicists, mineralogists, geologists and many other natural scientists serve as contact persons and conduct the necessary tests and examinations to provide valuable results. Many production problems at a customer's site can be solved, for example, by conducting causal analysis and working out solutions to address the source of the issue.



Our variety of service offerings

Your Benefits

We provide our customers with measurement results and interpretations that can be used to improve the quality and reliability of their products. This helps reduce downtimes and failure rates and leads to reliability and an increase in downstream customer satisfaction.

Our customers receive precise measurement results that enable them to create specifications for materials and components and to test them before they are deployed.

Testing boasts a high cost-benefit ratio, saving customers time and money while measuring with the technology best suited for the task at hand, all run by specialists.

For more information or to contact us, please visit https://analyzing-testing.netzsch.com/en/contract-testing.

Contract Testing

Table 1. Methods in our applications laboratory

Method	Recordable Information	Temperature Range	Gases	Sample Size*
Thermogravimetry	Mass changes, thermal stabilities	-180 to 2400°C	inert, oxidizing, reducing, static, dynamic, vacuum	Crucible volume: up to 5 ml
Differential Scanning Calorimetry (DSC)	Phase transformation temperatures and enthalpies, specific heat capacity	-180 to 1650°C	inert, oxidizing, reducing, static, dynamic	Crucible volume: up to 190 µl
High-Pressure DSC (up to 15 MPa, 150 bar)	Phase transformation temperatures and enthalpies, specific heat capacity	-50 to 600°C	inert, reducing, oxidizing, other gases on request	Crucible volume: up to 190 µl
Photo-DSC	Analysis of photo-initiated reactions, influence of UV stabilizers, UV-light curing	-100 to 300°C	inert, oxidizing, dynamic	Crucible volume: up to 85µl
Differential Thermal Analysis (DTA)	Phase transformation temperatures	-180 to 2400°C	inert, oxidizing, reducing, static, dynamic	Crucible volume: up to 900 µl
Simultaneous Thermal Analysis (STA)	Phase transformation temperatures and enthalpies, specific heat capacity, mass changes, thermal stability	-180 to 2400°C	inert, reducing, oxidizing, static, dynamic, vacuum	DSC: 190 µl DTA: 900 µl
Evolved Gas Analysis (EGA)	Characterization of gases emitted by means of MS, GC-MS or FT-IR, coupled to TGA or STA	-180 to 2000°C		on request
Dilatometry (DIL) and Thermomechanical Analysis (TMA)	Dimensional changes, coefficient of expansion, density changes	-180 to 2800°C	inert, oxidizing, reducing, vacuum	Standard size: 25 mm, Ø 6 mm*
Dynamic-Mechanical Analysis (DMA)	Visco-elastic behavior	-170 to 600°C	inert, oxidizing	on request
Heat Flow Meter (HFM) and Guarded Hot Plate (GHP)	Thermal conductivity of insulating materials	-20 to 90°C (HFM) -160 to 600°C (GHP)	GHP: inert, oxidizing or vacuum	HFM: 305 x 305 mm* GHP: max. 300 x 300 mm
Laser/Light Flash Methods (LFA)	Thermal diffusivity and thermal conductivity	-125 to 2000°C	inert, oxidizing, static and dynamic	Standard size: Ø 12.7 mm
Dielectric Analysis (DEA)	Curing behavior of reactive polymers	RT to 400°C		on request
Seebeck Coefficient (SBA)	Seebeck coefficient, electrical conductivity	-125 to 1100°C	inert, oxidizing, reducing	max. Ø 25.4 mm
Kinetics as a Service	Comprehensive kinetic evaluation, prediction and process optimization. Available for different methods incl. DSC, TGA, STA, DIL, etc.	depending on process	depending on process	depending on process
Rotational Rheometry	Shear viscosity, yield stress, thixotropy, visco-elastic properties, frequency and temperature sweep	-40 to 450°C	ambient, inert	on request
Capillary Rheometry	Shear and extensional viscosity, die swell, melt strength, pVT measurements	5 to 500°C	ambient, inert	on request

*special sample sizes on request

Determination of the Mass Change of Mouth-Nose Protection Materials Under the Influence of Humidity

Dr.-Ing. Roland Wetzel, Customer Training

Fig. 1. Cloth and FFP2 masks

Introduction

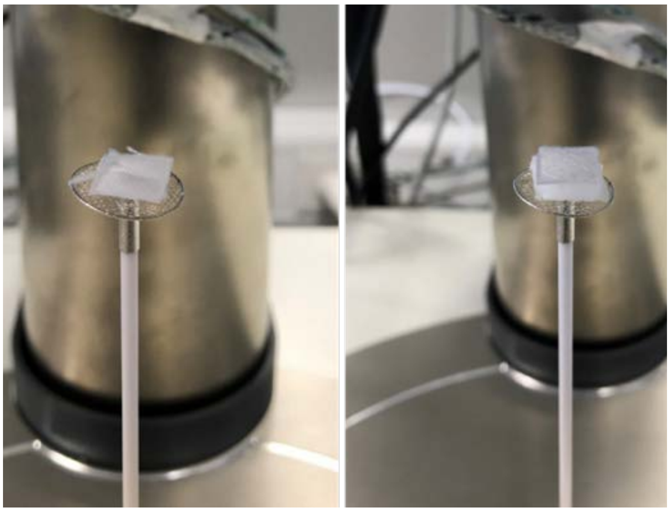
Since the worldwide spread of the SARS-COV-2 corona virus, mouth-nose protection has become part of our daily lives. Initially, bandanas, scarves and cloth masks were used in everyday life, but due to the rapid spread of the virus, they were replaced by medical masks. Once mouse-nose protection is put on, it is constantly in the wearer's inhaling and respiratory flows. Particularly the exhaling respiratory flow is nearly saturated with a humidity of 98% during exhaling [1].

As a result, the mask material is continually moistened, thus reducing the filter function. Furthermore, the humid environment promotes proliferation of harmful bacteria and fungi within the filter material and can lead to infectious respiratory diseases for the mask wearers. [2]

Due to the change from cloth to FFP2 masks, the structure changes from single-layer cotton fabric to multi-layer fleece and results in varying behavior during moisture adsorption. This difference can be excellently characterized with the help of thermogravimetric measurements at varying relative humidity contents.

Measurement Conditions

The two samples were prepared from the center part of an FFP2 and a cloth mask (Figure 1) and then investigated with an STA 449 ***F3*** *Jupiter*®, equipped with copper furnace and coupled to a proUmid humidity generator. In order to characterize the sample in line with their real operating conditions, they were aligned with the inner side of the mask facing the moisture flow (Figure 2).



a) b)

Fig. 2. Sample position on the Pt/Ir net of the sample prepared a) from the cloth mask and b) from the FFP2 mask

Measurement Results

Figure 3 depicts the TGA curves obtained as a function of temperature and relative humidity for the samples of both the cloth and FFP2 masks.

When looking at the TGA results for the cloth mask sample (black) in more detail, an average mass increase of 1.3 mg, corresponding to approximately 8%, could be detected following the increase in relative humidity of 40% to 90% at 32°C. This is caused by the adsorption of water on the sample. When the relative humidity is subsequently reduced to 40%, a residual load of up to 0.75% remains. Only when the temperature is increased to 80°C is the remaining moisture entirely released again. This adsorption and desorption behavior of the cloth mask sample for the 5 cycles is reproducible and reversible.

Also the TGA curve of the FFP2 mask sample shows a mass increase as soon as the relative humidity is increased to 90% at 32°C. However, the mass increase is significantly lower and is only about 0.2%, corresponding to about 0.04 mg. Reducing the relative humidity to 40% ensures complete release of the humidity adsorbed. In contrast with the cloth mask, a residual load cannot be clearly detected for the FFP2 mask sample. As a result, even the temperature increase to 80°C does not cause any further significant mass change.

Summary

While mouth-nose protection is worn, it is continually exposed to moist respiratory air. By investigating the mass change at different moisture content levels, conclusions can be drawn about the adsorption capacity or residual moisture load of the individual mask materials.

The cloth mask sample shows a stronger moisture penetration which is only released in its entirety at elevated storage temperatures. The temperature treatment at 80°C therefore ensures complete drying of the cloth mask and also prevents the spread of bacteria and/or fungi within the cloth.

Literature

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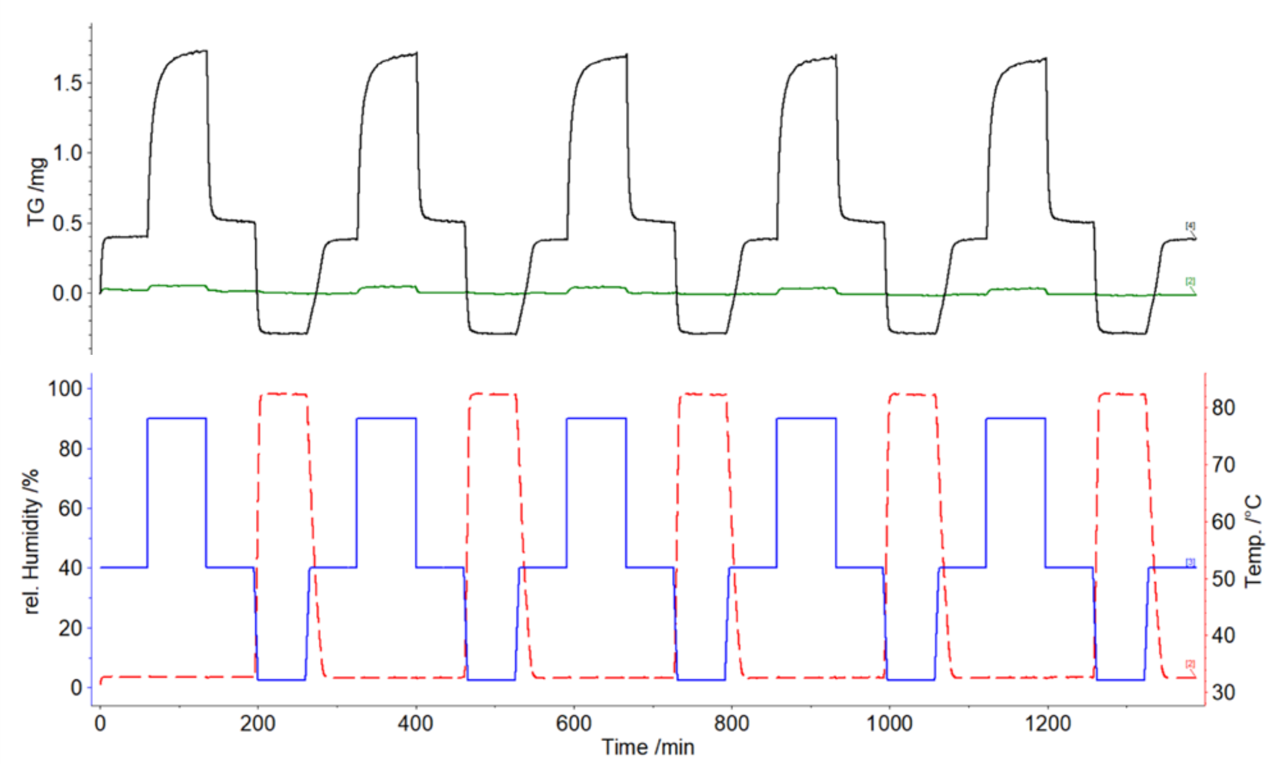


Fig. 3. TGA results as a function of the temperature program along with the relative humidity for the cloth mask sample (black) and the FFP2 mask (green).

Thermochemistry of Energy Storage Materials

Dr. Dmitry Sergeev and Dr. Michael Müller, Institute for Energy and Climate Research, Structure and Function of Materials (IEK-2), Forschungszentrum Jülich GmbH, Germany

Introduction

High-temperature processes and technologies, e.g., thermochemical conversion (combustion, gasification, and pyrolysis) of biomass, solid oxide cells and membranes, as well as high-temperature storage materials, require fundamental understanding of inorganic materials and their thermodynamic and thermophysical properties. The main properties of these materials can be represented with phase diagrams (structure, phase transition temperatures and concentration), formation and phase transition enthalpy, heat capacity, thermodynamic activity or Gibbs energy of solutions, composition and partial vapor pressure of the gas phase, density, thermal expansion and viscosity. All these properties can be combined in a consistent thermodynamic database, which is created according to the Calphad[1] approach (Figure 1). The combination of experimental results with the Calphad modelling enables description of relevant thermodynamic properties of multicomponent systems.

NETZSCH Instruments at FZ Jülich

To be able to cover all mentioned topics, in total 19 instruments for thermochemical analysis are used in our labs, which allow for obtaining thermodynamic

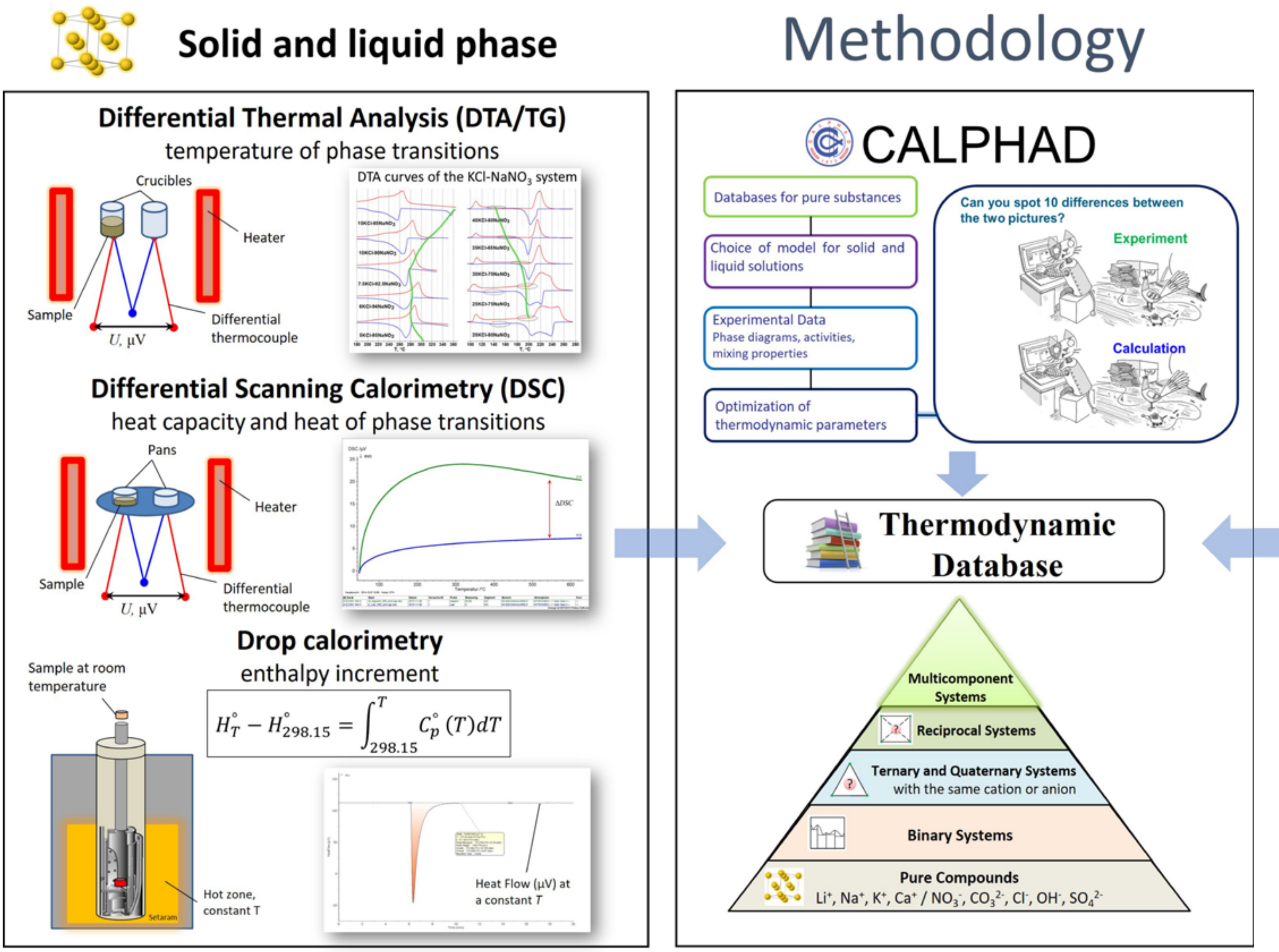


Fig. 1. Methodology for development of thermodynamic database

properties in a wide temperature range from -150°C to 2800°C. Nine of these DTA/TGA, DSC, DIL and SKIMMER/DTA/TGA instruments are supplied by NETZSCH (Figure 2).

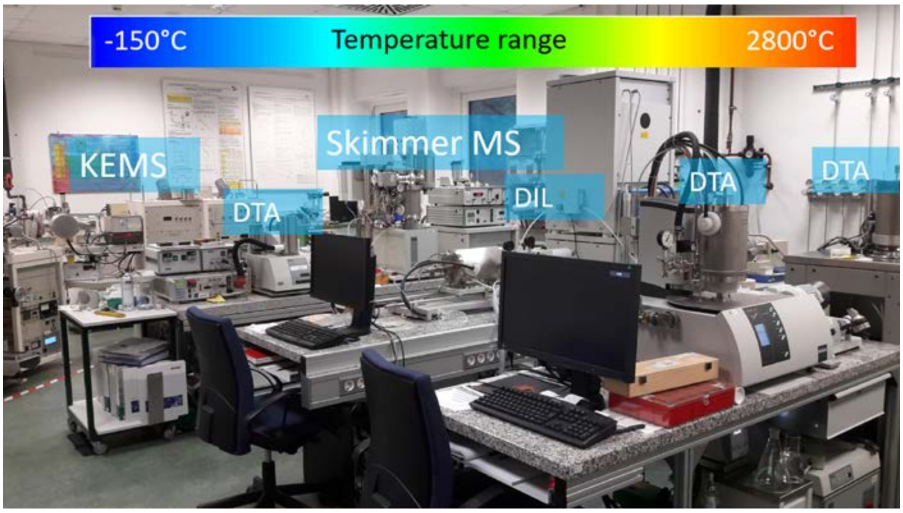
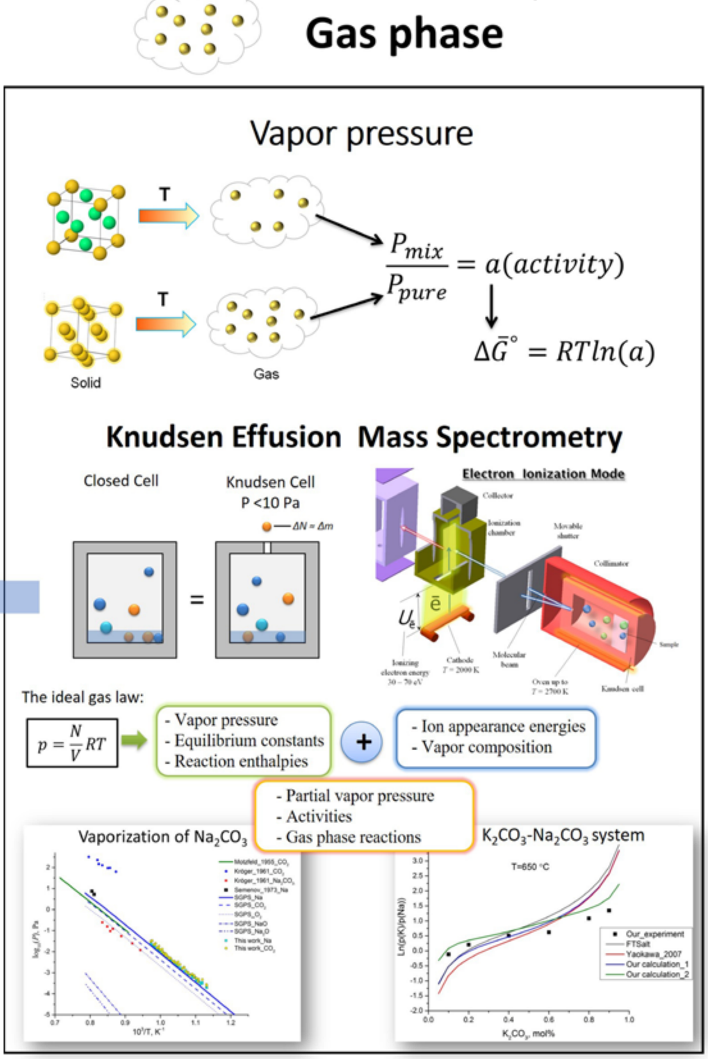


Fig. 2. One of the thermochemistry laboratories at IEK-2 of Foschungszentrum Jülich

PCM-Screening

One of our current projects is "PCM[2]-Screening 2: Evaluation of eutectic mixtures for use as PCM: Thermodynamic modelling and experimental methods", which is supported by the Federal Ministry for Economic Affairs and Climate Action on the basis of a decision by the German Bundestag within the project PCM-Screening (FKZ 03ET1441) and PCM-Screening 2 (FKZ 03EN6005D). In the frame of this project, we are working together with our project partners from BTU Cottbus, TU Dresden and GTT-Technologies from Herzogenrath. We are looking for suitable eutectic salt mixtures which can be used for high-temperature thermal energy storage applications.



Salt Systems – Continuous Electricity Feed

Salt systems are widely used as heat carriers or chemical reactants in many important industries, such as metallurgy, nuclear and solar energy. In contrast to photovoltaics and wind power, solar power plants offer the possibility of continuous electricity feed into the grid, independent of daily cyclical fluctuations in solar radiation intensity, through the integration of thermal storage systems.

For this project, the cheapest and most readily available salts have been selected: Na^+, K^+, Ca^{2+}, Mg^{2+} // Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}. The main requirements for selection of salt mixtures are high energy density, suitable phase transition temperature, good thermal conductivity, low temperature-dependent volume change, low volatility, and thermal and chemical stability.

---

[1] CALPHAD stands for CALculation of PHAse Diagrams, Computer Coupling of Phase Diagrams and Thermochemistry

[2] PCM stands for Phase change material, latent heat storage material

Thermal Stability by Means of STA

One of the first parameters which should be checked before starting thermodynamic studies of a system is thermal stability. It is important to know in which temperature range the system can be studied under open or closed conditions to prevent mass change of the sample. The simplest way to check this is to use TGA/DTA at some continuous heating rates, e.g., 5 K/min, which gives a quick overview of the sample (Figure 3). But in comparison to the thermodynamic equilibrium, where the heating rate of 0 K/min will be assumed, the heating rate of 5 K/min is quite high.

In thermodynamics, vapor pressure represents the thermal stability of the system, which can be described by the Hertz-Knudsen-Langmuir equation. Therefore, "stepwise TGA/DTA" (Figure 4) is a more informative approach than the continuous one.

It can be seen in Figure 4 that a vaporization rate of 0.02 mg/hour was detected at 400°C for $Ca(NO_3)_2$, which was measured with the STA 449 ***F3*** under an argon atmosphere. It should be noted that this value depends on the size of the orifice of the lid of a DTA crucible and the diffusion velocity of the gases. This value corresponds to the vapor pressure of around 10^{-2} Pa, which was measured in parallel by Knudsen Effusion Mass Spectrometry (KEMS) in our lab. The main species in the gas phase (NO, O_2 and NO_2) of the decomposition reaction of $Ca(NO_3)_2$ were detected. Temperature dependence of the vaporization rate based on TGA/DTA results for the decomposition/vaporization reactions of $Ca(NO_3)_2$, $NaNO_3$ and KNO_3 is presented in Figure 5 and can be considered according to the Clausius-Clapeyron equation. These results yield the possibility for determination and validation of the formation enthalpy in the thermodynamic databases.

Phase Transitions

By determination of phase transition temperatures of the ternary $Ca(NO_3)_2$-KNO_3-$NaNO_3$ system, supercooling effects were observed by DTA measurements. It was found that such mixtures form nitrate glasses and can be recrystallized by heat treatment close to the melting temperature. Figure 6 shows the 1st and 2nd heating DTA and DIL curves of the $43Ca(NO_3)_2$-$41(KNO_3)_2$-$16(NaNO_3)_2$ mixture.

In the 1st heating of the DTA measurement, an exothermic effect was observed which is related to recrystallization of the glass phase. It was possible to avoid this effect by using a special temperature program (isothermal heating at 100°C and slow cooling to room temperature). After reheating, the exothermic effect no longer occurred, which is proof that the initial components had reached equilibrium. The same temperature program was also used for the dilatometer measurements (Figure 6). It can be seen that the first heating curve (blue DIL signal) drops to a certain level,

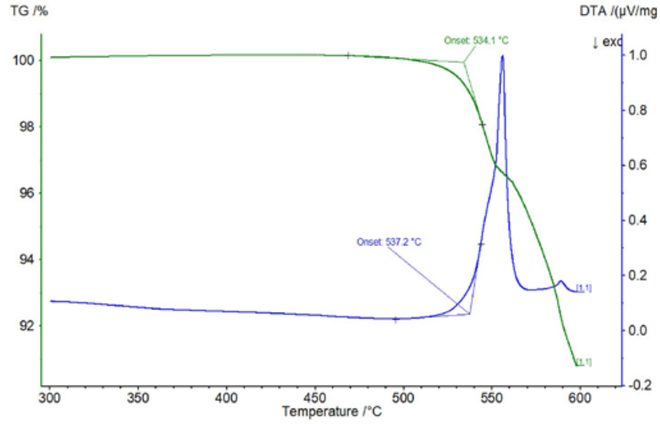


Fig. 3. Continuous TGA/DTA results for $Ca(NO_3)_2$

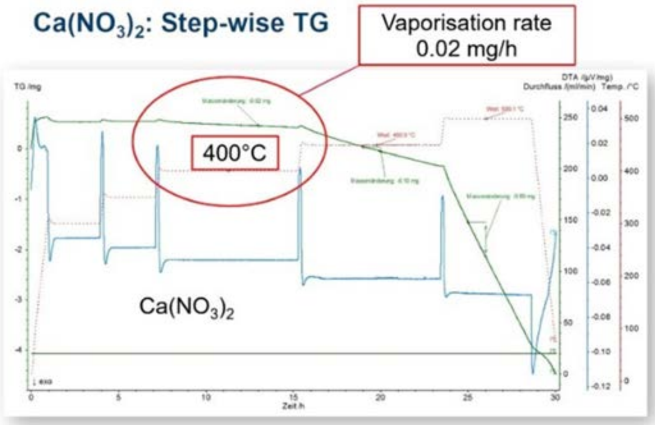


Fig. 4. Stepwise TGA/DTA results for determination of the vaporization rate of $Ca(NO_3)_2$

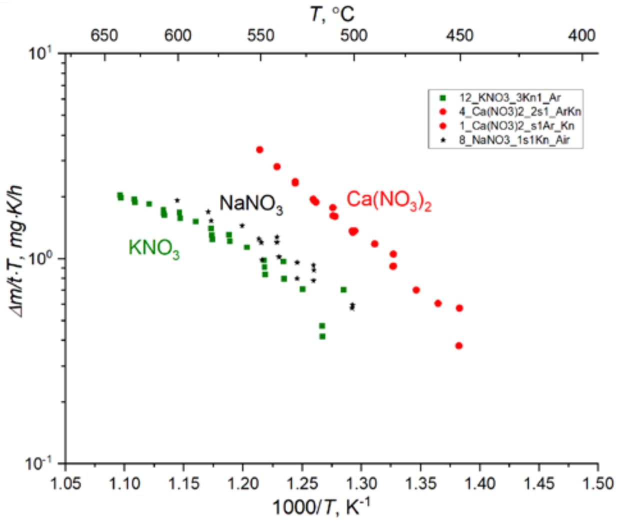


Fig. 5. Temperature dependence of vaporization rate based on TGA/DTA results for decomposition/vaporization reactions of $Ca(NO_3)_2$, $NaNO_3$ and KNO_3

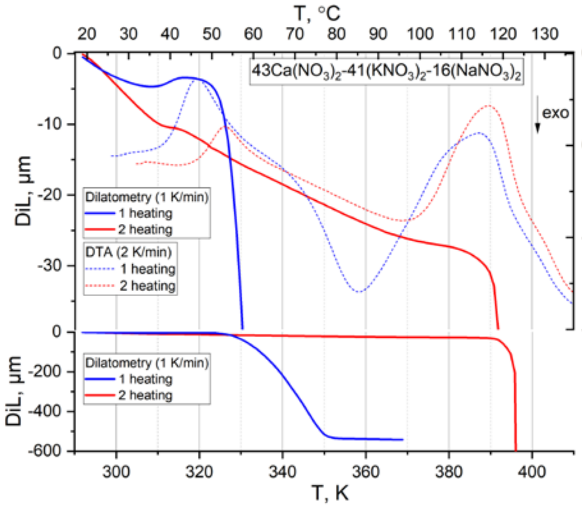


Fig. 6. DTA and DIL results for the 1st and 2nd heating of the $43Ca(NO_3)_2$-$41(KNO_3)_2$-$16(NaNO_3)_2$ mixture

indicating shrinkage of the sample associated with the exothermic DTA effect. The second DIL heating curve (red DIL signal) shows a slow shrinkage of the sample below 110°C; after that, the signal decreases rapidly because of complete melting. The obtained melting temperature of the sample was detected to be 124°C.

Conclusion

These examples show just a small part of the obtained results and the necessity of combining different techniques for better understanding of thermal effects of materials. A more detailed description of our studies of salt systems can be found in the following publications under References [1-8].

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The Interface Matters! GC-MS Coupling with the New External VAB300x

Dr. Michael Schöneich, Applications Scientist

Fig. 1. STA 449 ***F1*** *Jupiter*® with GC-MS coupling and the VAB300x valve box

Introduction

One cannot imagine the world of material analysis without the combination of thermogravimetry (TGA) and evolved gas analysis (EGA). Simultaneous investigation of thermally induced mass changes and the associated outgassing products allows for deeper insight into the origin of the material behavior observed and ultimately results in better understanding of the material properties and their potential applications.

Along with the well-established direct coupling approaches by means of infrared spectroscopy (TGA-IR) and mass spectrometry (TGA-MS), coupling to a GC-MS system represents another possibility.

Interface

The main challenge in coupling two instruments does not so much involve coordinating the functionality of the individual instruments, but rather overcoming the differences between the two methods.

This can be achieved with a coupling interface that has been specially designed for this demanding task, such as the new NETZSCH VAB300x valve box (Figure 1.) This is characterized by the following features:

- GC-MS-manufacturer-independent coupling set by means of an external interface
- Simple technical connection to the GC-MS system by means of integration via the standard S/SL injector
- "All in One" principle – integration of the necessary peripherals (e.g., pump, filter, gas control)

Principle of the Coupling

Based on a heated outlet system of the TGA, the outgassing products are transferred to the interface by means of a heated transfer line. The interface itself consists of a 2-position switch valve, which can be heated to a maximum temperature of 350°C and which allows for a defined gas volume (up to 500 µl) to be exchanged between the two gas flows separated from each other (Figure 2).

This enables easy transfer of outgassing products of the thermobalance into the carrier gas flow of the GC-MS system.

VAB300x for GC-MS Coupling

Once the outgases arrive at the GC-MS, the gas mixture will be separated into the individual gas components (Figure 2) based on its physical interaction with the column material and subsequently analyzed by means of mass spectrometry.

Example

The TGA-GC/MS coupling features the capability of also separating complex gas mixtures into their individual components. This makes it particularly well suited for the analysis of complex samples or reactions such as those occurring, for example, in polymers, biomass, pharmaceuticals and foods.

As an example, Figure 3 shows the outgassing chromatogram of instant coffee, described in Application Note 230 "How to Detect Residual Caffeine in Decaffeinated Instant Coffee". Along with the main compotent, caffeine, a variety of compounds – mostly aromatic – can be detected, which traditionally cannot be distinguished with a direct method (MS/IR).

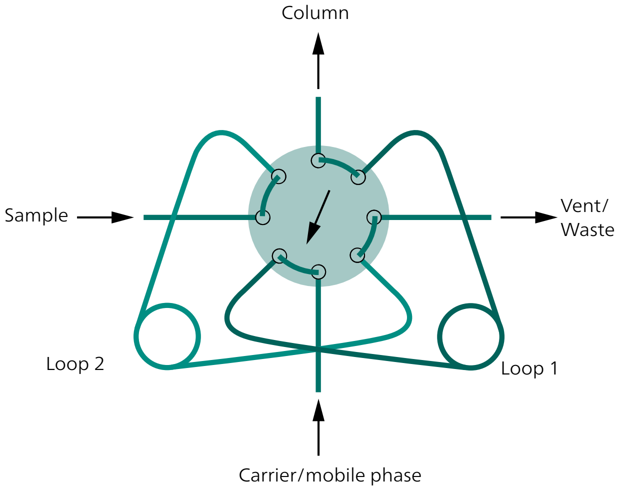


Fig. 2. Operating principle of the VAB300x

Further information can be found in Application Note 230 → http://netzs.ch/AN230_EN

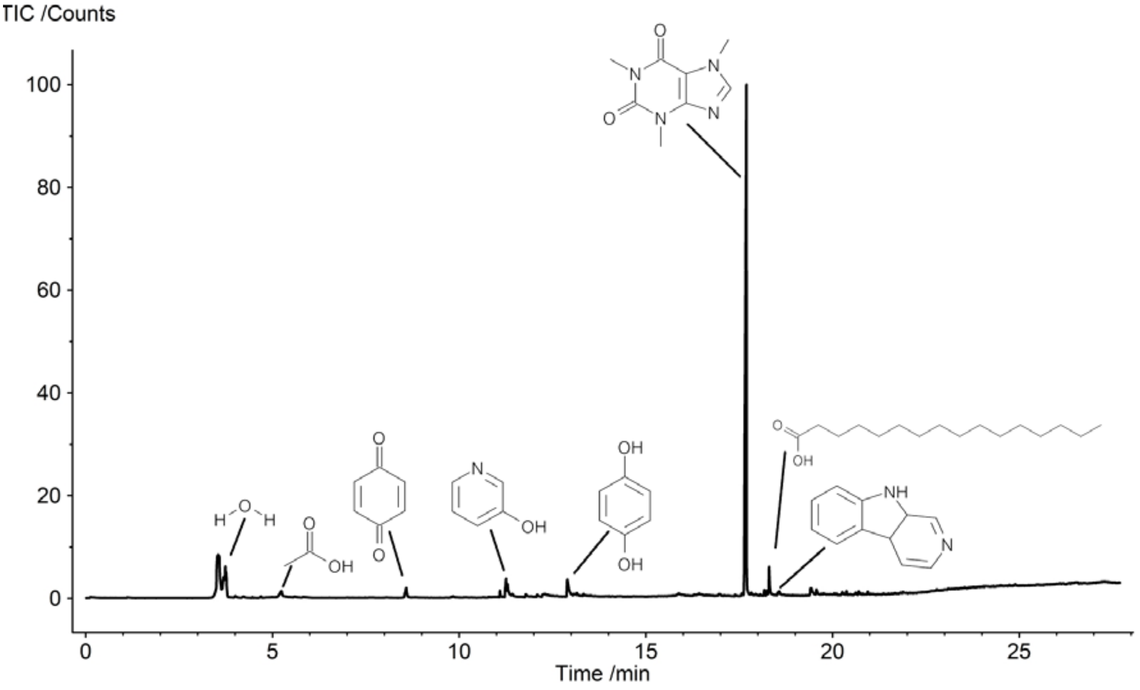
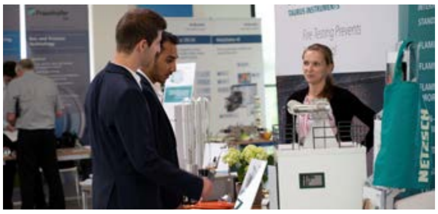


Fig. 3. Outgassing chromatogram of instant coffee from Application Note 230

Events & More

60 YEARS ANNIVERSARY of NETZSCH-Gerätebau GmbH



In 2022, we've been proud to be spending the whole year celebrating our 60th anniversary together with you. Each month, we've featured one of our devices and highlighted the course of its development and related applications by sharing some exciting and entertaining stories from 60 years of NETZSCH Analyzing & Testing. You can find all these fun stories on our blog or easily and conveniently via the QR code.

Besides these entertaining stories, we also took the opportunity on the occasion of our 60th anniversary year to host an in-house exhibition at our company headquarters in Selb on July 4, 2022.

Along with interesting presentations from both external, renowned companies and internal speakers, offering insights into current research topics and technological solutions, there there were ample opportunities for our numerous visitors to get to know our thermoanalytical instruments, talk to product specialists and take a guided tour through our applications laboratory.

For us, it was the best exhibition of this outstanding year and it will certainly not be the last such in-house event at NETZSCH.

We would like to invite you already today to the next event of this kind and look forward to welcoming you in Selb!

Meet Us – Virtually!

You can register for all webinars free of charge on our website. Below is a small selection for January, February and March.

January 19, 2023:
Speaker: Dorothea Stobitzer
Topic: High-Temperature Applications

February 7, 2023:
Speaker: Dr. Elena Moukhina
Topic: Thermal Risk Management

March 22, 2023:
Speaker: Markus Hehn
Topic: STA (Basic Introduction, Measuring Principle, Instrumentation, etc.)

Please find more webinars at:
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Events & More

Reshaping Tomorrow Together

In May, we had the great pleasure of hosting the first NETZSCH FUTURE DAYS. They were an exciting mix of lectures and interviews in the field of materials science. The four core topics were:

- Pharma & Life Science
- Batteries & Insulations
- Smart Manufacturing & Smart Labs
- Additive Manufacturing

With this interesting mix of topics, we hope to have brought all those in attendance a few steps closer to surmounting their future material challenges and are pleased to have had them with us on this thought-provoking journey toward reshaping tomorrow together.

Missed our FUTURE DAYS? You can still watch the presentations under the following link or QR code:
https://www.futuredays-netzsch.com/en

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