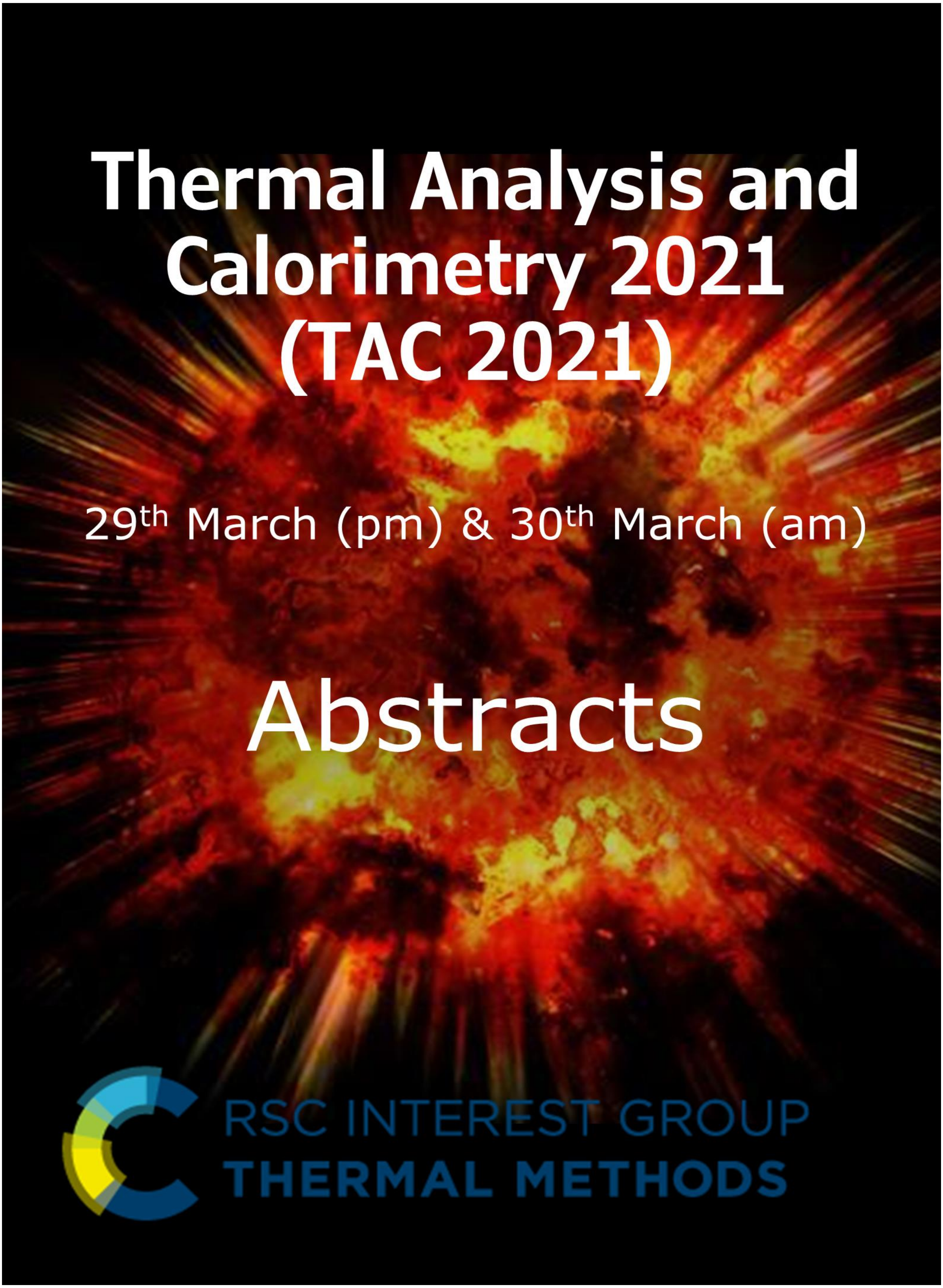


# Thermal Analysis and Calorimetry 2021 (TAC 2021)

29th March (pm) & 30th March (am)

# Abstracts

RSC INTEREST GROUP
THERMAL METHODS

# Oral presentations

## Dielectric behaviour of water at sub-ambient temperatures: A Commemorative Lecture in Memory of Glynn Van-de-Velde

G Van-de-Velde and J C Duncan*
Lacerta

My colleague, Glynn Van-de-Velde started this work as a means to identify and check the freshness of fish using dielectric thermal analysis. Much work has been carried out on frozen food, especially fish, where glass transition temperatures have been reported[1]. Dielectric measurements are particularly sensitive to water, due to its large relative permittivity. Therefore, it has an advantage over DSC and DMA techniques. During the course of investigations, it became evident that the relaxations observed at low temperature were, in fact, due to water itself. This prompted a study of amorphous water present in ice and the activation energy for the observed relaxations has been calculated. Consequently care should be taken using results from frozen samples containing water, as the observed behaviour could in large part be due to that of water itself.

My presentation shall include a brief summary of my dear colleague's career.

I. Tolstorebrov∗, T.M. Eikevik, M. Bantle, A DSC study of phase transition in muscle and oil of the main commercial fish species from the North-Atlantic, *Food Research International*, **55** (2014) 303–310

# Dynamic Mechanical Analysis and its role in assessment of state of preservation of collagen –containing cultural heritage objects

M Odlyha* C Theodorakopoulos, G Foster, R Campana, N Cohen, A Bartoletti, A Bridarolli and L Bozec
Birkbeck, University of London

The low temperature relaxation transition of hydrated collagen containing material and of water as measured by dielectric (DETA) and dynamic mechanical (DMA) analysis and reported in work performed by Glynn Van-de-Velde has led to a review of part of our DMA database on collagen containing materials. This was established about 15 years ago within a collaborative project also involving conservators. Four categories of damage were established in historical parchments on the basis of differences measured by DMA and complementary spectroscopic (FTIR) and imaging techniques (AFM). Samples were made available from collections from diverse European archives. Unaged modern and accelerated aged samples were also tested. For the thermal DMA data one set of criteria used to establish damage was based on the behaviour of the low temperature (β) relaxation peak. A difference in temperature occurred in this peak for the historical samples, and after first heating from -150 to 150 °C a pronounced shift occurred to higher values on re-heating from -150 °C to 220 °C. The magnitude of this difference between the 1st and 2nd heating was found to vary with extent of damage in the sample. It appears from current literature that this low-temperature relaxation peak in collagen and other hydrated proteins has been widely studied particularly by dielectric techniques and it is generally accepted that the amplitude of this process decreases with decreasing hydration levels and is related to water in the hydration shell of the protein [1]. So current literature has provided a new understanding of this peak and highlighted that the damage assessment criteria we developed are associated with hydration processes. It is known that historical parchment absorbs more water than modern parchment arising possibly from differences in extent of denaturation of collagen. The structural change will affect its ability to interact with water molecules and also how they will be accommodated in the structure, as the proportion of collagen and gelatine in the sample changes. This lies at the basis of our damage assessment criteria and is supported by AFM images which display alterations in collagen D-banding as well as localised areas of gelatinisation and loss of structure.

[1] Kurzweil-Segov, Y., Popov,I., Solomonov, I., Sagit, I and Feldman, Y., Dielectric Relaxation of Hydration Water in Native Collagen Fibrils *Journal of Phys.Chem.B* **121** (2017) 5340-5346 https://doi.org/10.1021/acs.jpcb.7b02404

# Mixtures of halloysite clay nanotubes and wax for the consolidation of archaeological woods

Giuseppe Cavallaro*, Lorenzo Lisuzzo, Giuseppe Lazzara, Stefana Milioto
University of Palermo

The combination of natural polymers and clay nanoparticles represents a green strategy for the treatment of artworks. Within this, novel protocols for the consolidation of waterlogged archaeological woods were developed by mixing halloysite clay nanotubes (HNTs) and wax. In particular, halloysite/beeswax dispersions in acetone and halloysite/paraffin wax Pickering emulsions in water were tested as consolidant mixtures for wooden artworks. Preliminary investigations on beeswax/halloysite composites at variable composition were conducted in order to determine their thermal and mechanical properties by using thermogravimetry (TG), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). DSC data revealed that the HNTs addition generates a reduction of the beeswax crystallinity. On the other hand, DMA results showed that the presence of the nanotubes confers to the beeswax an inorganic skeleton, which preserves their elastic properties to a temperature range wider than that of pure beeswax. As concerns halloysite/paraffin wax Pickering emulsions, the optimization of the preparation procedure was supported by both optical microscopy and scanning electron microscopy, which allowed us to study the morphological and structural characteristics of the prepared hybrid materials. Micro-differential scanning calorimetry (µ-DSC) was conducted in order to investigate the thermodynamics of the melting of wax entrapped within the Pickering emulsions. We observed a reduction of the melting enthalpy due to the presence of the nanotubes, which partially destroy the crystallinity of paraffin. Moreover, the deconvolution of the µ-DSC thermograms allowed us to discriminate the two distinct phase transitions of wax melting, highlighting that the increase of the HNTs concentration decreases the contribution of the solid−metastable solid phase transition. The consolidation efficiencies of the halloysite/wax mixtures (acetone dispersions and aqueous Pickering emulsions) were estimated by studying the shrinking volume and the mechanical properties of the treated archaeological woods. Both consolidation protocols generated a strong reduction of the shrinking volume with respect to the untreated woods in agreement with the penetration of the consolidants within the pores of the wooden samples. A strong enhancement of the mechanical properties (elastic modulus, stiffness and stress at breaking point) of the woods were detected after their consolidation with HNTs/wax Pickering emulsions.

# Quantification and characterisation of water within drug-eluting beads

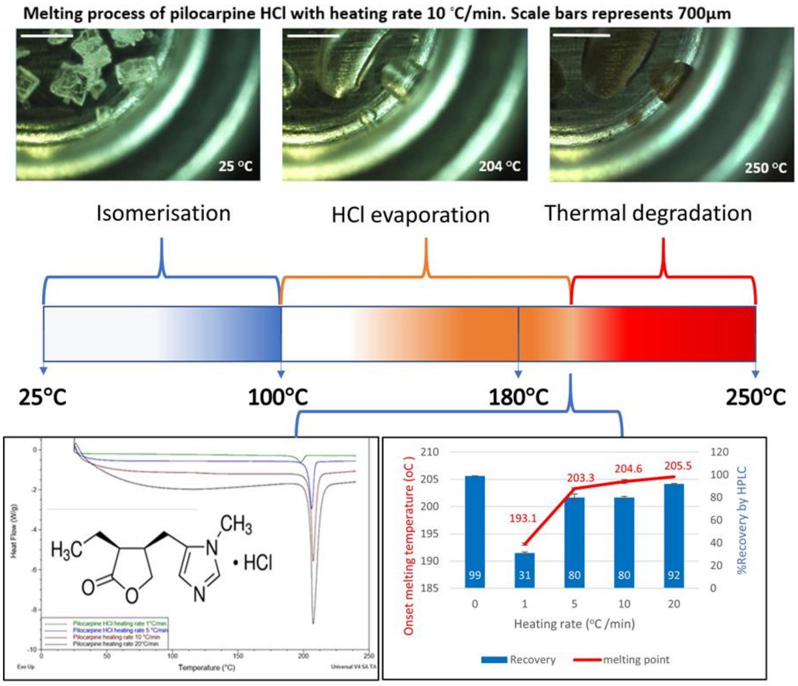
S Ahmad, A L Lewis, G M B Parkes, Y Tang, L J Waters*
University of Huddersfield

This work describes the analysis and characterisation of polymer beads, specifically focussing on the quantitative and qualitative aspects of water within such beads in the absence and presence of three model drugs, namely doxorubicin, imipramine and irinotecan. The size of the beads in the presence of increasing amounts of imipramine decreased as water was displaced, demonstrating the presence of drug-bead interactions. Thermogravimetric analysis (TGA) permitted determination of the total water content within the beads, ranging from beads alone that contained 96.8 % water, through to beads formulated with irinotecan that contained only 91.7 % water. Differential scanning calorimetry (DSC) was utilised to investigate water present within their hydrogel structures, separated into bound (non-freezing), loosely bound and unbound forms. For imipramine and irinotecan beads there was little impact on the relative ratio of bound, loosely bound and free water within the structure. For doxorubicin and the higher drug loaded irinotecan a distinct decrease in overall water content was seen. This study confirms the ability of TGA and DSC to characterise the differing types of water within the beads and indicates the relative changes in water content in the presence of model drugs.

# Pharmaceuticals – they all degrade and that’s why thermal analysis is important

Paul Royall
King’s College, London

The measurement of melting points is vitally important in pharmaceutical development. Melting point is a critical material attribute which reflects drug purity, drug quality, drug stability and informs medicine formulation strategies. It is a prerequisite for the development of a new medicine or drug product as this vital parameter is required for inclusion in an investigational brochure. Melting points may be used in a predictive capacity, for example Chu & Yalkowksy (2009) have shown that drug absorption may be related to melting point. And lastly, characterising the melting of phase change materials is vital for the development of better cool packs which are used in the support of cold chain logistics. The aim of the presentation is to show that the application of heat often leads to degradation through a melt and as a consequence the talk will provide some recommendations to aid melting point determination and thermal analysis. The paper concludes with a five-stage approach for the melting point measurement of heat sensitive drugs. The stages are 1) visually observe melting; 2) measure mass during melting; 3) measure melting points at different heating rates; 4) measure the extent of chemical degradation during the melt; 5) analyse potential isomerisation or any pre-melt reactions.



Malallah, Osamah S., Basilia Hammond, Taha Al-Adhami, Asma Buanz, Abdulmalik Alqurshi, William D. Carswell, Khondaker Miraz Rahman, Ben Forbes, and Paul G. Royall. "Solid-state epimerisation and disproportionation of pilocarpine HCl: Why we need a 5-stage approach to validate melting point measurements for heat-sensitive drugs." *International journal of pharmaceutics* 574 (2020): 118869.

# Determination of the equilibrium enthalpy of melting of two-phase semi-crystalline polymers by fast scanning calorimetry

Clément Fosse, Antonella Esposito*, Laurent Delbreilh
Université de Rouen

Polymers can crystallize to different extents, but never entirely. The equilibrium enthalpy of melting $\Delta H_m^0$ $[J \cdot g^{-1}]$ is an extrapolated thermodynamic quantity attributed to crystallizable macromolecules and widely used to characterize polymers in their semi-crystalline state, for it allows estimating the degree of crystallinity by direct comparison with the enthalpy of melting obtained from differential scanning calorimetry. $\Delta H_m^0$ is typically determined by cross-comparing the results obtained by at least two techniques. This work proposes a simplified experimental protocol to estimate the value of $\Delta H_m^0$ by using Fast Scanning Calorimetry (FSC). This approach applies to any crystallizable polymer for which a specific microstructure can be obtained (*i.e.* a two-phase semi-crystalline microstructure with a negligible amount of rigid amorphous fraction) and that can also be quenched to its fully amorphous state. Such a two-phase microstructure can be obtained on nanoscale samples through an annealing process performed *in situ* on the FSC sensor at crystallization temperatures as close as possible to the melting temperature. The enthalpy of melting is then evaluated from the two-phase model for different crystallization times (*i.e.* different crystallinities) and the value of $\Delta H_m^0$ is obtained by extrapolating the data to the theoretical 100% crystalline state. This procedure was applied on samples whose values of $\Delta H_m^0$ are already available in the literature, but also on more recent bio-based polyesters whose thermal properties are still under investigation.

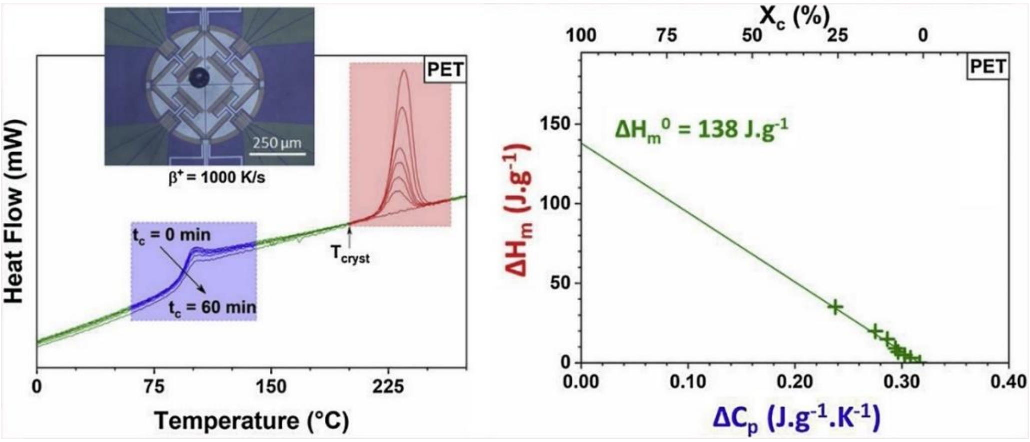


**Figure 1.** Illustration of the method used to estimate the value of $\Delta H_m^0$ of crystallizable polymers by Fast Scanning Calorimetry. Nanoscale samples were crystallized *in situ* on FSC sensors at selected crystallization temperatures for increasing crystallization times (left); the melting enthalpy measured during the subsequent heating ramp was plot against the heat capacity step at the glass transition (right); the extrapolation provided an estimate of the equilibrium enthalpy of melting $\Delta H_m^0$.

[1] Fosse C., Bourdet A., Ernault E., Esposito A., Delpouve N., Delbreilh L., Thiyagarajan S., Knoop R.J.I., Dargent, E. Determination of the equilibrium enthalpy of melting of two-phase semi-crystalline polymers by fast scanning calorimetry, *Thermochim. Acta,* ***2019****, 677, 67-78.* https://doi.org/10.1016/j.tca.2019.03.035

# Nitroglycerine; a simple molecule which highlights some of the challenges with the thermal analysis of energetic materials

Ruth Tunnell*
QinetiQ

Nitroglycerine (NG) was first synthesised by the Italian chemist Ascanio Sobrero in 1847 but it remains one of the most important and frequently used components of energetic materials [1], including gun and solid rocket motor propellants.

There are a number of advantages to using NG in formulations. For example, it is a highly energetic plasticiser which has green chemistry credentials and it is easily desensitised which makes it more straightforward to handle than might be expected.

However, for a simple molecule, NG has a number of challenges. It is adversely affected by trace amounts of water and acid which can lead to its rapid decomposition, making synthesis and its subsequent analysis on a small scale difficult.

This review will provide examples of the challenges with regards to the thermal analysis of NG. As will be shown, these are indicative of the types of problems generally encountered during the thermal analysis of energetic materials.

[1] Köhler, J., Meyer, R., *Explosives* Fourth revised and extended edition, VCH, 1993

# HFC Studies on Conventional and Novel energetic materials

Amanda Catherall*, Mark Penny, Matthew Didsbury
BAE Systems

Heat Flow Calorimetry (HFC) has been used (STANAG 4582 and 4147) to measure the stability and compatibility of propellant materials, however, very little is known about the full capability of the technique. With the move towards ‘insensitive/lower vulnerability’ materials do the STANAG methods still work for novel propellant materials? Is HFC a suitable technique for studying stability of novel energetic materials?

A TA instruments TAM IV has been installed at BAE Systems, Glascoed; the first TAM IV to be installed within the UK Energetics community.

A down-selection of 15 propellants covering a range of different formulations were chosen as test samples for this piece of work. This selection involved a mix of conventional and novel formulations, including single base, triple base, RDX based and HMX based formulations to identify any differences in behaviour/heat flow as the samples are artificially aged.

HFC studies have been carried out in the temperature range 70 – 89 °C in accordance with STANAG 4582. Conventional propellants behave as expected, allowing stability/compatibility measurements to be carried out.

Preliminary results show that STANAG 4582 is not a one-size fits all method. Novel propellant materials do not fulfil the heat flow requirements of STANAG 4582 to be able to determine shelf-life. This work will focus on the suitability of the method for novel propellant materials. Further work is to establish a method to study the stability and compatibility of pyrotechnic and secondary explosive materials.

# The Power of Model-Fitting Kinetic Analysis: Reconciling the Kinetics of Bicyclo-HMX Thermolysis in Solid State and Solution

Nikita V. Muravyev*, Igor N Melnikov, Konstantin A Monogarov, Ilya V Kuchurov, Alla N Pivkina
Russian Academy of Sciences

Thermal decomposition of cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (Bicyclo-HMX) both in solid state and in solution has been studied with a set of thermal analysis methods. Differential scanning calorimetry data obtained at several heating rates was analysed using the model-fitting kinetic technique. The kinetic parameters for a non-catalytic stage of thermolysis in solution are found to be $E_a = 168.7 \pm 1.4$ kJ mol$^{-1}$, log (A, s$^{-1}$) = 15.7 ± 0.2, to prove the activation energy agrees with the theoretical prediction of the barrier for N–$NO_2$ bond rupture in BC-HMX molecule. Thermal decomposition of solid BC-HMX is shown to be much more complex. The formal three-step kinetic scheme is proposed, which explains the numerous experimental findings (thermal behaviour at various confinement degree, morphology changes under heating) and the previous literature results as well. The first step of the process obeys a third-order nucleation-growth model with the $E_a = 186.6 \pm 1.2$ kJ mol$^{-1}$ and log (A, s$^{-1}$) = 16.7 ±0.3. Overall, the strength of the performed model-fitting kinetic analysis is demonstrated and the extension of the proposed methodology to other energetic materials with complex decomposition patterns is suggested.

# Thermal analysis of magmas – extreme hazards, extreme challenges

Hugh Tuffen
Lancaster University

The thermodynamic and transport properties of magma underpin the formation of the Earth's crust, hazardous volcanic processes, and related resources from ore deposits to geothermal heat. Magma is a high-temperature, multiphase mixture of liquid, crystals, and vapour, whose behaviour is governed by phase transitions occurring over timescales from milliseconds to millions of years. Key processes including crystallisation, volatile exsolution, and sintering are readily characterised *via* thermal analysis, yielding useful constraints on magma dynamics.

I will provide an overview of ongoing thermal analysis of magmas, including my own work using simultaneous thermal analysis (TGA-DSC-MS) and heated stage microscopy to characterise volatile exsolution and crystal growth/fusion within lavas. There is ample scope for collaboration between volcanologists and material scientists, and future challenges will be highlighted, including high-pressure experimentation and the characterisation of extremely rapid transitions.

# Enhanced $CH_4$ Hydrate Formation using Hybrid MOF plus Promoter System

Jyoti Shanker Pandey*, Qian Ouyang, Nicolas von Solms, Professor
Technical University of Denmark

Metal-Organic Framework (MOFs) are functional porous material having an open metal site with organic linkers. MOFs are of very low density and high surface area. The application of MOFs in gas hydrate is very recent, and there are many unknown. Due to the high surface area, MOF can improve the gas-liquid interface area, thus total gas stored in the hydrate. In this research, we have used a high-pressure differential scanning calorimeter to investigate the total CH4 gas storage in hydrate in the presence of HKUST-1. Effect of different chemicals, including Amino acids Methionine, Surfactant Sodium dodecyl sulfate, was studied and compared with pure water. Experiments were carried out at constant pressure P = 95-100 bar to investigate total gas capture under different liquid/solid ratio.

Results show improvement in gas storage in hydrate in promoters' presence at a given pressure and L/S ratio. Crystals were found to remain stable over multiple formations and dissociation cycles, suggesting high reusability. Additional discussion will be provided during the presentation.

# Method to Perform Microcalorimetry Measurements of Carbon Dioxide Adsorbing onto Ceria Nanopowders

A F Macdonald*, B J Smith, R M Harker
AWE plc

This paper presents the development of a method to measure the adsorption calorimetry of a gaseous species on a nanopowder. The method utilises a 1 $cm^3$ stainless steel ampoule (containing the nanopowder) connected to a microreaction perfusion unit and held within a Heat Flow Calorimeter (HFC). Argon is continuously flowed (20-100 ml/hr) through the ampoule (held at 80 °C) and periodically a small aliquot (6.9 $cm^3$ STP) of the carbon dioxide adsorbate is introduced into the flow. Thermal events are identified when the reactant gas reaches the cerium dioxide nanopowder (ceria) and the off-gas is subsequently fed to an infra-red spectroscopy gas cell to determine how much carbon dioxide gas has been consumed. Experiments are carried out at atmospheric pressure.

The gas line is of all metal design up to the perfusion unit to allow for increased confidence in gas purity. A method has also been developed to allow the ceria to be pre-treated in an argon furnace and then introduced into the perfusion unit under argon. Thermal events are typically identified within 10 minutes of the aliquot being added and a delay time of 70 minutes is generally required between doses to allow the heat signal to return to a baseline level (depending on argon flow rates). The HFC can provide data that relates the aliquot size of the $CO_2$ added to the thermal event but the data is not yet ideal due to insufficient mixing of the reagents. Options for improvements will be discussed.

The study was also supported by a variety of other characterisation techniques including Brunauer-Emmett-Teller surface area determination, scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, diffuse reflectance infra-red spectroscopy and thermo-gravimetric analysis – mass spectrometry to identify the adsorbed species (carbonates, hydrogen carbonates and carboxylates) formed when carbon dioxide reacts with ceria surfaces.

**Keywords:** Heat Flow Calorimetry,

Adsorption, Carbon Dioxide, Ceria,

Infra-Red Spectroscopy

# Manufacturers’ flash presentations

## Hiden Analytical Company Profile

### Michael Thomas, Hiden Analytical

Hiden Analytical have been designing and developing the highest quality quadrupole mass spectrometer-based gas analysis systems for over 30 years. We have built a reputation for delivering instruments with superior sensitivity, accuracy and reproducibility together with a first-class global service and applications support network. From dedicated triple filter UHV TPD quadrupoles to atmospheric plasma characterisation systems, Hiden have developed a range of analytical mass spectrometers that address the most advanced and demanding applications.

# How Temperature-Controlled Experiments Aid Materials Characterisation

Robert Gurney

Linkam Scientific Instruments

Temperature influences the behaviour of all materials, so it is important to have precise control of the working temperature during any experiment. This is particularly important when observing the effect of temperature on material properties; for example the effectiveness of a pharmaceutical compound at body temperature, the behaviour of cells when vitrified at -196 °C or the stability of a metal alloy at 1500 °C.

In this presentation, two examples of how temperature control is used in experimental analysis will be discussed: cryopreserved human prostate cancer cells at <-195 °C, and a study of phase formation in Cr–Co–Ni alloys at 800 °C.

# See what is really happening within your furnaces

Olivier Savard
Hitachi

Although thermal analysis techniques like DSC, STA, DMA and TMA have been around for a long time, it's always been a challenge to know what is happening to the samples during measurements. From colour to dimension changes, being able to see how the sample behaves when heating or cooling can add important information to the thermal analysis story. Visible images can also be used as a valuable troubleshooting tool to explain unusual behaviours during an experiment. Using real examples, this presentation will go through the information thermal analysis users could gain when being able to see their samples while using thermal analysis techniques (DSC, STA and DMA). Examples of how to work with results combining images and thermal analysis data will also be shown to highlight the power of images combined with thermal analysis and what type of information could be extracted from visible images (*e.g.* RGB values) will also be presented.

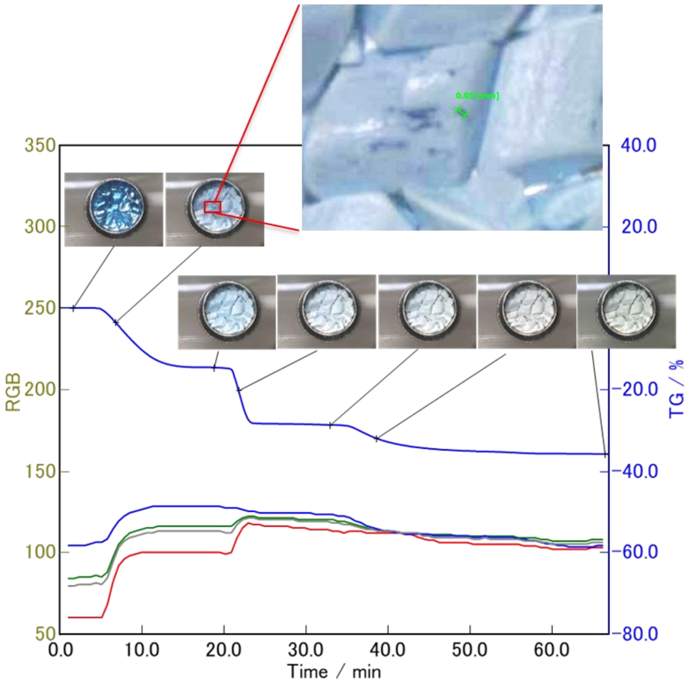


*Figure 1: Images and colour analysis combines with TGA measurement.*

# Latest Thermal Analysis Developments at Setaram

David Dale*, Derek Black
Setaram

This presentation will highlight some of the recent developments in thermal analysis at Setaram with particular emphasis on custom solutions for special applications.

## Mettler Toledo flash DSC: rapid-scanning DSC

Joe Marsh

Mettler Toledo

# Latest Developments from TA Instruments

Jas Mahey

TA Instruments

Snapshot of latest developments at TA, which include:

- The Discovery X3 DSC, which allows the simultaneous measurement of 3 samples versus a common reference – for increased throughput and statistical evaluations
- The TAM Micro XL battery calorimeter, which allows the measurement of electrochemical reactions which occur within batteries and affect stability, efficiency, and life cycles. It complements an existing set of battery calorimeters available for the TAM (Thermal Activity Monitor)
- The HP TGA, which is the only commercially available bench top high pressure TGA system, capable of operating under corrosive atmospheres and steam, making it ideal for biomass gasification studies, accelerated corrosion studies and decom and use in fume hoods

# Solid state epimerisation in α-lactose monohydrate by optical DSC and NMR

Thamer Alzoubi*, Garry P. Martin and Paul G. Royall
King’s College, London

Lactose is a popular excipient that is available in many forms and frequently used in many medicines. Although considered chemically stable in its solid form, when in aqueous solution, lactose suffers rapid mutarotation. So, it is surprising that no consideration has been given to the possibility that the monohydrate may induce epimerisation when it passes through the powder bed, as alpha lactose monohydrate suffers dehydrate during heating. Therefore, the aim of this study was to investigate the anomeric content of α-lactose monohydrate and β-lactose during thermal analysis. Initially, NMR gave the β content of both samples as 3.7 ±1% and 85.7±1%, respectively. DSC analysis was stopped post hydrate desorption (160 °C) and post re-crystallisation (190 °C). The anomeric composition of α-lactose monohydrate increased to 11.6±0.9% and 29.7±0.8% β-anomer ($p<0.05$). Whereas no changes were observed with the anhydrous β-lactose. Epimerisation continued to increase with isothermal conditioning, reaching a maximum of recorded content of 29.1±0.7% to β-anomer after 190 °C. Hyphenated optical microscopy was incorporated during the DSC analysis providing new information regarding the possible degradation of lactose powders and epimerisation commencing at solid-state. Change of colour was observed at the melting point of α-lactose monohydrate, 214.2 ±0.9 °C. Whereas, anhydrous β Lactose demonstrated discolouration at the solid-state 223 °C (m.p 234.2 °C). Therefore, the previously described ‘recrystallization’ peak was unambiguously confirmed to be epimerisation and the loss of hydrate molecule initiated the epimerisation of α-lactose monohydrate.

# Design and Thermal and Spectroscopic Characterization of novel architecture’s POSS nanoparticles

Ignazio Blanco
University of Catania

Polyhedral oligomeric silsesquioxanes (POSSs), with Si vertices interconnected by –O– linkages, form three-dimensional nanometer size cage structures with substituents attached to silicon atoms. These substituents may contain reactive groups, such as hydroxyl or isocyanate. A combination of a rigid inorganic nanocore with organic vertex groups makes POSS molecules useful hybrid building blocks that can be chemically incorporated in the polymer matrix by copolymerization, grafting or reactive blending, or physically mixed by solvent casting or polymer processing by using, for example, the extrusion technique [1]. The use of POSSs for making polymer composites has grown exponentially since the last few years of the 20th century. In comparison with the other most commonly used fillers, POSSs possess the advantage of being molecules. Thus, this allows us to combine their nano-sized cage structures, which have dimensions that are similar to those of most polymer segments and produce a particular and exclusive chemical composition. These characteristics linked with their hybrid (inorganic–organic) nature allow researchers to modify POSS according to particular needs or original ideas, before incorporating them into polymers [2].

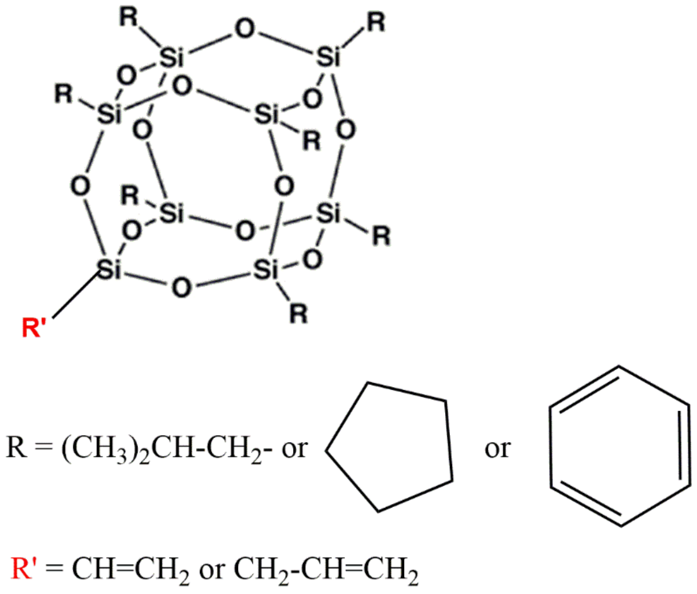


Figure 1. Molecular structure of the prepared and investigated POSSs

In this context, our research group at the University of Catania, in collaboration with eminent researchers in the field, tested the stabilization of different polymers, synthetics or naturals, such as polyethersulfone (PES), ethylene propylene diene monomer (EPDM), polyethylene oxide (PEO), and chitosan by the incorporation of polyhedral oligomeric silsesquioxanes (POSS) molecules [3-6]. Represented in their most common form by the symbol T8 and having a diameter usually falling in the range of 1.5–3 nm, POSS molecules comprise a silicon and oxygen cage completed by organic groups that are covalently bonded with silicon atoms. Novel architectures of POSS with various organic groups were synthesized by using corner capping reaction in order to verify their polimeryzability in the presence of monomer. In this work, after a spectroscopic investigation aiming at verify that the obtained molecules have the structure for which they were designed, their thermal behavior in terms of resistance to thermal degradation were evaluated by means of thermogravimetric analysis (TGA). The obtained temperatures at 5% mass loss (T5%) were compared with each other and with those of the POSSs previously designed and studied by us.

[1] Lichtenhan, J.D., Pielichowski, K., Blanco, I. POSS-Based Polymers. Polymers 2019, 11, 1727

[2] Blanco, I. The Rediscovery of POSS: A Molecule Rather than a Filler. Polymers 2018, 10, 904.

[3] Cicala, G., Blanco, I., Latteri, A., Ognibene, G., Agatino Bottino, F., Fragalà, M.E. PES/POSS Soluble Veils as Advanced Modifiers for Multifunctional Fiber Reinforced Composites. Polymers 2017, 9, 281

[4] Zaharescu, T., Blanco, I., Bottino, F.A. Antioxidant activity assisted by modified particle surface in POSS/EPDM hybrids. Appl. Surf. Sci. 2020, 509, 144702

[5] Legnani, L.; Iannazzo, D.; Pistone, A.; Celesti, C.; Giofrè, S.; Romeo, R.; Di Pietro, A.; Visalli, G.; Fresta, M.; Bottino, P.; et al. Functionalized polyhedral oligosilsesquioxane (POSS) based composites for bone tissue engineering: Synthesis, computational and biological studies. RSC Adv. 2020, 10, 11325–11334

[6] Stipanelov Vrandečić, N., Erceg, M., Andričić, B., Blanco, I., Bottino, F.A. Characterization of poly(ethylene oxide) modified with different phenyl hepta isobutyl polyhedral oligomeric silsesquioxanes. J. Therm. Anal. Calorim. 2020, 142, 1863–1875

# Dilution enthalpies of $LiBO_2$ and $LiB_5O_8$ aqueous solutions at 298.15 K and the application of ion-interaction model

Fei Yuan*, Long Li, Yafei Guo, and Tianlong Deng
Tianjin University of Science and Technology

Boron and its compounds play an important role in modern energy and material sciences including permanent magnetic, superconducting, boride cermets, boron-based fuel-rich propellants and borate whisker materials. Lithium metaborate is a high-quality piezoelectric material for mobile communication, and lithium pentaborate can be used as a high quality laser material and so on. In order to establish the thermodynamic model of brine systems and to utilize the valuable salt lake resources effectively and comprehensively, heat enthalpy knowledge on the salt lake system containing lithium and borate ions is of great significance not only to understand the ion-interaction between solute-solvent and solute-solute as well as the effects of ion strength, temperature on excess free energy, but also to provide fundamental data in predicting the crystallizing and evaporating behaviors of these salt lakes. Studies on the thermodynamic properties of the salt lake brine systems containing lithium and borate ions is of great significance to establish the solubility predictive model of electrolytes to promote the industrial exploitation of those valuable salt lake resources effectively and comprehensively. The dilution enthalpies of $LiBO_2$ (aq) from 0.1 to 0.8 $mol \cdot kg^{-1}$ and $LiB_5O_8$ (aq) from 0.3 to 0.9 $mol \cdot kg^{-1}$ at 298.15 K and 101.325 kPa were investigated using the microcalorimeter BT 2.15. The apparent molar enthalpies on the two species of lithium borates were obtained on the basis of experimental data, and then the diagrams of their apparent molar enthalpy against molality for $LiBO_2$ (aq) and $LiB_5O_8$ (aq) were also plotted. According to Pitzer ion-interaction equations, the Pitzer single-salt parameters ($\beta_{MX}^{(0)L}$, $\beta_{MX}^{(1)L}$, $\beta_{MX}^{(2)L}$, $C_{MX}^{L}$) for $LiBO_2$ and $LiB_5O_8$ were obtained, which are not reported in the literature. The calculated apparent molar enthalpies for $LiBO_2$ (aq) and $LiB_5O_8$ (aq) agree well with the experimental values, which indicate that the Pitzer single parameters of $LiBO_2$ and $LiB_5O_8$ obtain are reliable.

# Investigation on the Structure, Thermal Stability, Degradation Behavior of Polylactic acid-Based Composite Fibers Regulated by Protein using Thermal Analysis

Hanling Gu*, Hao Liu, Bowen Cai, Qianqian Deng, Fang Wang
Nanjing Normal University

Blending the two materials can overcome and improve the poor performance of single-phase materials, give full play to the advantages of each phase, and obtain composite materials with different uses. In this work, dual crystallizable poly(L-lactic Acid)/silk fibroin biological tissue engineering composites with unique pore structure were prepared by electrospinning method. DSC and TMDSC were used to analyse their crystallinity, movable amorphous and rigid amorphous part composite nanofibers with different thermal histories. The morphology and thermal degradation behaviour of the nanofibrous composites were observed and studied by SEM and TGA, respectively. Simultaneously, enzyme degradation experiments were conducted in vitro. This study provides a theoretical basis for regulating the thermal stability, degradability, mechanical properties and biocompatibility of materials by understanding the effects of crystal structure on the microstructure and macrostructure of materials.

# Dilution enthalpies of $LiBO_2$ and $LiB_5O_8$ aqueous solution at 308.15 K and the application of ion-interaction model

Hua Li*, Fei Yuan, Long Li, Yafei Guo and Tianlong Deng
Tianjin University of Science and Technology

Borates have been used generally in numerous fields and are regarded as crucial materials, which have great applications in lithium battery electrolyte solutions, whisker materials, laser materials and other high technology domains. The measurement of the heat of dilution at a single temperature is not sufficient to support the investigation of the interaction between ions. Therefore, it is very important to develop the dilution heat and apparent molar enthalpy of binary systems ($LiBO_2 + H_2O$) and ($LiB_5O_8 + H_2O$) at 308.15 K. The enthalpies of dilution have been measured for aqueous $LiBO_2$ solutions from 0.0412 to 0.1237 mol·kg$^{-1}$ and $LiB_5O_8$ from 0.0539 to 0.1212 mol·kg$^{-1}$ at 308.15 K and 101.325 kPa were investigated using the microcalorimeter TAM IV. The relative apparent molar enthalpies on two lithium borates were obtained, and relative partial molar enthalpies of the solvent and solute, $\bar{L}_1$ and $\bar{L}_2$ were calculated and the diagrams of their apparent molar enthalpy against molality for $LiBO_2$ (aq) and $LiB_5O_8$ (aq) were also plotted. The thermodynamic properties of the complex aqueous solution were represented with a modified Pitzer ion-interaction model and the ($\beta^{(0)L}_{MX}$, $\beta^{(1)L}_{MX}$, $\beta^{(2)L}_{MX}$, $C^{L}_{MX}$)for $LiB(OH)_4$ and $LiB_5O_6(OH)_4$ were obtained.

Keywords: Lithium borates; dilution Enthalpy; Relative apparent molar enthalpy; Ion-interaction model

# Osmotic coefficients and water activities for the ternary system ($LiB(OH)_4$ + $Li_2B_4O_5(OH)_4$ + $H_2O$) and its binary subsystems at 288.15 K: Isopiestic measurement and Pitzer model

Kaiyu Zhao*, Yafei Guo, Lingzong Meng, Nelson Belzile, Tianlong Deng
Tianjin University of Science and Technology

Osmotic coefficients and water activities for the binary systems ($LiB(OH)_4$ + $H_2O$), ($Li_2B_4O_5(OH)_4$ + $H_2O$) and the ternary system ($LiB(OH)_4$ + $Li_2B_4O_5(OH)_4$ + $H_2O$) at 288.15 K and ambient pressure were determined by the isopiestic method using a modified gravimetric isopiestic apparatus. Meanwhile, the specific formation progress and geochemical characteristics of two hydrated lithium borates minerals discovered in a natural salt lake brine were elaborated in terms of water activity. Then the hydrated interactions of ions with $H_2O$ in aqueous $LiB(OH)_4$ and $Li_2B_4O_5(OH)_4$ solution systems were compared at the molecular level. The Pitzer model was selected to describe the thermodynamic properties of the aqueous systems containing different species of lithium borates, then the Pitzer single salt parameters $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and $C^{\phi}$ for the binary systems ($LiB(OH)_4$ + $H_2O$) and ($Li_2B_4O_5(OH)_4$ + $H_2O$) and mixing ion-interaction parameters $\vartheta_{\mathrm{B(OH)_4,\ B_4O_5(OH)_4}}$ and $\psi_{\mathrm{Li,\ B(OH)_4,\ B_4O_5(OH)_4}}$ for the ternary system ($LiB(OH)_4$ + $Li_2B_4O_5(OH)_4$ + $H_2O$) were fitted with the experimental water activities and osmotic coefficients using the multiple linear regression method. And the water activities of the ternary system were calculated using the Pitzer parameters, and the calculated water activities of this ternary system agree well with the experimental values, which indicates that the Pitzer parameters obtained in this work are reliable. Eventually, the fundamental thermodynamic data and Pitzer parameters obtained and presented for the first time in this work are essential for further revealing the thermodynamic properties of lithium borates minerals.

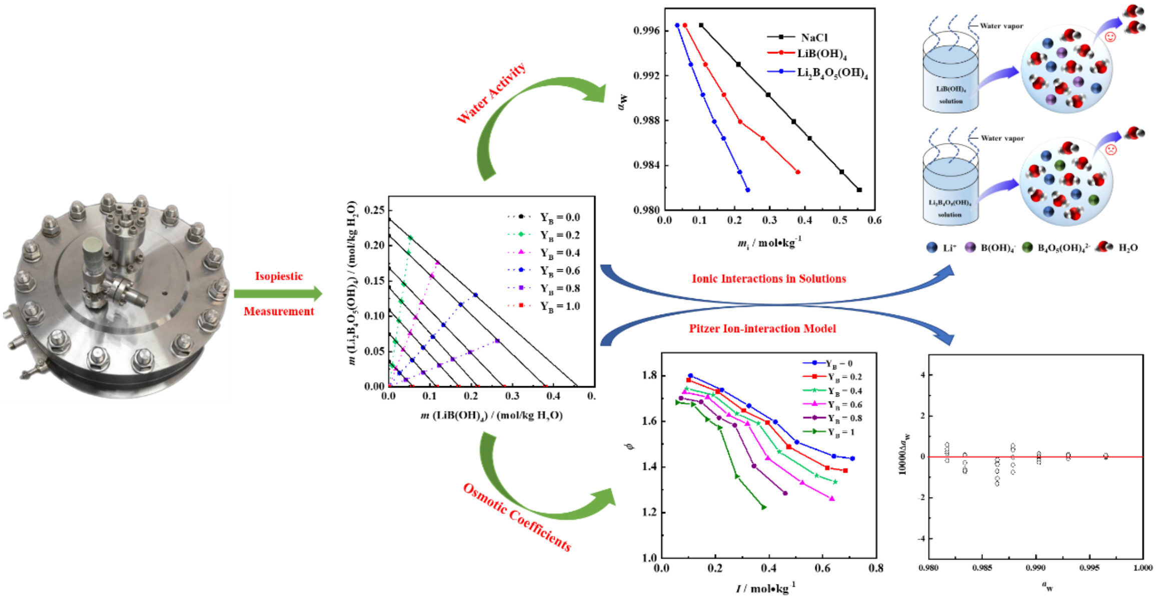


Figure 1. Isopiestic investigation, thermodynamic data and model for the ternary system ($LiB(OH)_4 + H_2O$) and ($Li_2B_4O_5(OH)_4 + H_2O$)

***Key words:*** Lithium borates; Water activities; Osmotic coefficients; Pitzer model.

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# Volumetric properties and the ion-interaction parameters of the binary system ($CsB_5O_8 + H_2O$) at temperatures from (283.15 to 363.15) K and 101 kPa

Kangrui Sun*, Hanyu Zheng, Yafei Guo, Lingzong Meng, Tianlong Deng
Tianjin University of Science and Technology

Salt-lake brines with high concentrations of cesium and boron in the west regions of China are well known around the word and contain many kinds of hydrated cesium borates due to the complex structure of B – O bonds. Reliable data on physical properties such as density and apparent molar volumes are of interest to develop separation and purification process for minerals, as well as partial molar volumes of electrolytes can provide valuable information about the structural interactions for the ion – ion, ion – solvent and solvent – solvent. It is highly desirable to study the thermodynamic properties of apparent molar volumes and construct a thermodynamic model for the binary systems containing cesium and borates.

The densities of $CsB_5O_8$ (aq) in the range of salt concentrations from 0.02526 to 0.08148 $mol \cdot kg^{-1}$ were determined by an accurate Anton Paar Digital vibrating-tube densimeter at 5 K intervals from 283.15 to 363.15 K and 101 kPa. The apparent molar volume ($V_\phi$), the coefficient of thermal expansion ($\alpha$), apparent molar expansibility of the solute ($\phi_E$) were calculated and variations of these properties against temperature and concentration were revealed minutely. According to Pitzer ion-interaction apparent molar volume model of aqueous electrolyte system, the Pitzer single salt parameters i.e. $F_{MX}$ ( $\beta^{(0)v}_{MX}$ , $\beta^{(1)v}_{MX}$ and $C^{v}_{MX}$ , M = $Cs^+$, X = $[B_5O_6(OH)_4]^-$), the temperature-dependence equation [$F_{MX}$ ($i$, $p$, $T$) = $a_1 + a_2\ln(T/298.15) + a_3(T-298.15) + a_4/(620-T) + a_5(T-227)$, $i = \beta^{(0)v}_{MX}$ , $\beta^{(1)v}_{MX}$ and $C^{v}_{MX}$ ] as well as their coefficients $a_i$ ($i$ = 1 to 5) in the binary system were obtained, which is not reported in the literature. The fitted results of single salt parameters $\beta^{(0)v}_{MX}$ , $\beta^{(1)v}_{MX}$ and $C^{v}_{MX}$ were in good agreement with the experiment values, indicating that the single salt parameters and temperature relational coefficients for $Cs[B_5O_6(OH)_4]$ obtained in this work are reliable.

***Keywords:*** Cesium pentaborate; Density; Apparent molar volume; Pitzer model

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# Thermal Analysis and Infrared Spectroscopy as Complementary Methods for Assessing the State of Preservation of Collagen in Collections of Archaeological Bones

Chloe Pearce*, Marianne Odlyha
Birkbeck, University of London; English Heritage

English Heritage collections contain extensive numbers of archaeological bones from animals such as cattle, sheep and pig going back to Roman times. In a recent collections' audit over 10% of their bone and ivory objects were designated to be in poor condition. This is intrinsically linked to their physical state and condition of preservation of the main chemical components in bones *i.e* organic (collagen) and inorganic (hydroxyapatite) which will be influenced by both burial conditions and those following their excavation, such as the environmental conditions on storage and display.

Thermogravimetric analysis has been used to measure overall organic and inorganic content, by calculating the weight loss between 200 and 800 °C. Infrared spectroscopy has been used to determine the presence and state of preservation of collagen and the percentage of collagen within the bone. The organic content as determined from TGA can provide information on the organic contamination as well as the mineral content. Both proteinaceous and non-proteinaceous compounds can enter the system during the diagenesis process.

The data also indicates a link between the collagen percent content and its degradation. Samples that demonstrate a higher collagen percentage which is also less damaged also demonstrate higher overall preservation. This pattern illustrates a relationship between site and collagen preservation, extending to correlate geographic location with preservation. Sites located along the southern British show from the measurements a worse state of preservation, whereas those in the north of the country show a better state of preservation.

Thermogravimetric analysis and infrared spectroscopy have been used to give an overview of collagen content of the samples and state of preservation, also of the mineral content. This information has been used to select samples for recent neutron radiography experiments and to advise conservators, collections staff and curators on individual needs of objects.

# Interrelations of activation energies in thermoanalytical kinetics

Peter Šimon*, Tibor Dubaj, Zuzana Cibulková
Slovak University of Technology

Condensed state processes are extensively studied by thermoanalytical methods. Mechanisms of these processes are very often unknown or too complicated to be characterised by a simple kinetic model. They tend to occur in multiple steps that have different rates. To describe their kinetics, the single-step approximation mathematically expressed in the form of general rate equation is mostly applied [1]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\,f(\alpha) \tag{1}$$

Eq. (1) is called the general or generalized rate equation. Among the methods based on Eq. (1), the isoconversional (or model-free) ones are most popular, mainly in evaluation of the experimental results obtained from measurements carried out under linear heating rate.

In papers published, it can be very often encountered that the experimental results are evaluated by several methods and the results are mutually compared. Flynn–Wall–Ozawa [2, 3] (FWO), Kissinger–Akahira–Sunose [4] (KAS) and Starink [5] methods belong to this group. All the methods reside in the treatment of kinetic results by the relationship

$$\ln\left(\frac{\beta}{T^a}\right) = -b\frac{E}{RT} + c \quad \Rightarrow \quad \ln\beta = -b\frac{E}{RT} + a\ln T + c \tag{2}$$

where $\beta$ is the heating rate, $T$ is the isoconversional temperature, $E$ is the activation energy and $a$, $b$, $c$ are constants. The values of constants $a$, $b$, $c$ depend on the approximation applied for the calculation of temperature integral [1]. The activation energy is obtained from the slope of the dependence $\ln(\beta/T^a) = f(1/T)$. If one takes into account the $a$ and $b$ values for individual methods, by differentiation of $\mathrm{d}(\ln\beta)/\mathrm{d}T$ can be obtained:

$$1.058E_{\mathrm{FWO}} = E_{\mathrm{KAS}} + 2RT = 1.0037E_{\mathrm{Starink}} + 1.8RT \tag{3}$$

From Eq. (3) it can be seen that the activation energies from FWO, KAS and Starink methods are interrelated, and it makes no sense to make far-reaching conclusions from their comparison. The authors also frequently overlook that the differences between the methods are below the uncertainty of $E$. Apart from "deterministic" differences in the $E$ values given by Eq. (3), different transformations applied to experimental data in these methods lead to additional random scatter in the resulting $E$ values, thus making their comparison even more meaningless. Moreover, it is to bear in mind that all the three methods mentioned here are integral and they can be mathematically incorrect in the case of variable activation energy [6].

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# Can be used DSC to study PET bottles?

Lucie Šudomová*, Helena Doležalová Weissmannová, Jiří Kučerík
Brno University of Technology

In this study, we focused on verifying that the use of differential scanning calorimetry (DSC) can lead to the identification of polyethylene terephthalate (PET) bottles with a specific composition.

As some studies suggest, PET properties depend on its microstructure and are determined by crystallization rate, the degree, and quality of crystallinity. DSC parameter (glass transition, crystallization, and melting behavior of PET) depend on crystallinity, which varies depending on the use of different feedstock types. Hence, the parameters from DSC should correspond to the PET composition.

In general, the types of bottles investigated in this work can be divided into three groups according to their history. The largest group are bottles made entirely of virgin PET. The second group contains bottles containing additives, which improve barrier properties. However, these additives act as contaminants during recycling. Therefore, it is necessary to find a way to identify them and find a way to exclude them from the recycling stream. The third group represents bottles that contain a certain amount of recycled material – recycled PET (rPET) or PET made from natural sources (bioPET). PET in this group is currently of great interest due to European Union plans that will oblige producers to use these types in PET bottles. Besides, declaration of use rPET/bioPET in bottles is already a marketing advantage due to some consumers' preference. However, the proof of rPET/bioPET in a PET bottle is a great challenge.

The results suggest that the combination of DSC data and advanced statistical methods can divide analyzed bottles into these three categories. Bottles from virgin PET shown similar properties and can easily be identified. PET bottles with additives are a challenge due to different additives, but there is potential for their identification. The data also showed that some bottles declared to contain rPET/bioPET may, in fact, not contain these PET types. We conclude that DSC has a great potential to become a robust method for identifying PET bottles' different chemical compositions.

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# Reversing and non-reversing contribution to the melting of HDPE-GNPs nanocomposites

Evangelia Tarani*, Christoph Schick, George Vourlias, Dimitrios N. Bikiaris, Konstantinos Chrissafis
Aristotle University of Thessaloniki

Recently, there has been a growing interest in nanocomposites applied in thermally conductive polymeric materials. Polymers that are highly conductive and electrochemically active have been focused on some promising applications such as solar cells, sensors, energy storage devices, and pipes. Polyethylene (PE) is a low-cost semi-crystalline polymer that shows good thermal and mechanical properties and high chemical resistance. In certain areas, PE use is limited by its own mechanical and gas barrier properties, poor heat resistance, and low thermal and electrical conductivities, among others. Graphene nanoplatelets (GNPs), have been proposed as the next-generation multifunctional nanofiller for the improvement in matrices because of their high mechanical, thermal, and gas barrier properties. The objective of this work is to prepare HDPE/GNPs nanocomposites filled with different diameter sizes by the melt-mixing method. Crystallization and melting of HDPE/GNPs nanocomposites in non-isothermal conditions were studied at several cooling rates by using conventional differential scanning calorimetry (DSC) and Fast Scanning Calorimetry (FSC). The primary and secondary crystallization kinetics of HDPE was characterized as a function of the cooling rate. The approach to describe primary crystallization is based on temperature-dependent nucleation and growth of spherulites governed by an Avrami-type equation. An isoconversional technique was used to evaluate the apparent activation energy of the nanocomposites during the crystallization process far from thermodynamic equilibrium. Temperate Modulated DSC analysis (TM-DSC) was also employed to comprehend the melting behavior and separate the simultaneously occurring events during the melting of the samples. The non-reversible heat flow indicates that crystals undergo recrystallization during heating as a result of the metastable crystals formed by the cooling treatment. The reversing contribution was found to be broader and smaller in magnitude than the total and non-reversing curves and it exhibits multiple overlapped melting peaks. Such a transition is often impossible to detect with the conventional DSC scan due to the offset of the recrystallization exotherm and the melting endotherm. The presence of multiple peaks is attributed to the overlapping of melting and crystal reorganization in the same temperature range as classically observed in different semi-crystalline systems and to the presence of different populations of crystal sizes.

# Viscosity of $Ag_x((GeS_2)_{50}(Sb_2S_3)_{50})_{100-x}$ glass-forming system

Včeláková M*, Košťál P, Honcová P
University of Pardubice

Chalcogenide glasses are materials that have great application potential. Due to their properties, they can be used as optical fibres, sensors, lenses or in integrated circuits and in rewritable memories. [1, 2]

One of the most important property of glass-forming material is viscosity. The knowledge of viscosity is important for glass working, manufacturing or long-term stability of glasses. Viscosity also affects the cold crystallization in undercooled melt region. In principle, measuring of viscosity is not a complicated process. The issues can be long experimental time of measurements or cold crystallization of samples.

The viscosities in this work were measured using thermomechanical analyser (TMA) and two experimental methods, penetration, and parallel-plate method. The penetration method (cylindrical and hemispherical indenters) was used in the interval $10^7$ - $10^{13}$ Pa·s. The parallel-plate method was used for the interval of $10^5$-$10^8$ Pa·s. [3]

The viscosity measurements were performed on silver doped chalcogenide glasses and undercooled melts. Samples of $Ag_x((GeS_2)_{50}(Sb_2S_3)_{50})_{100-x}$ system (x = 0; 5; 7.5; 10) were prepared by classical melt-quenching method. On these samples, the viscosity was measured by both mentioned methods. It is necessary to know the coefficient of thermal expansion to determine viscosity by the parallel-plate method. These coefficients were also determined by use of TMA. Appropriate viscosity equation was used to fit the experimental viscosity data. Glass transition temperatures were determined from temperature dependence of viscosity and thermal expansion data. Kinetic fragilities were also determined and discussed.

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# Activity coefficients of sodium nitrate and cesium nitrate in aqueous mixtures using an electromotive force method at 298.15 K

Yanqin Meng*, Fei Yuan, Jiangtao Song, Yafei Guo, and Tianlong Deng
Tianjin University of Science and Technology

Electrolyte solutions are widely found in marine, geotechnical, and other fields, as well as in the engineering of inorganic chemistry and hydrometallurgy, and in nature. It is essential to study the mean activity coefficients of electrolyte solutions for the design, development of processes such as salt industry and desalination and it is of great significance to determine the activity coefficients of salt solution parts in salt industry. Activity coefficients for the ternary system of $NaNO_3$-$CsNO_3$-$H_2O$ were determined at 298.15 K by electromotive force (EMF) measurements of the cell: Na ion-selective electrode (ISE) | $NaNO_3(m_A)$, $CsNO_3$ $(m_B)$ | $NO_3$ ion-selective electrode (ISE) and over total ionic strengths from 0.01 to 4.5 $mol\cdot kg^{-1}$ for different ionic strength fractions (0, 0.1, 0.2, 0.4, 0.6, 0.8). The experimental data were interpreted by using the Harned rule and the Pitzer model. According to the Nernst equation, the mean activity coefficients in the mixed solution were calculated. Using multiple linear regression fitted the Pitzer mixed ion parameters $\vartheta_{Na,Cs}$ and $\psi_{Na,Cs,NO_3}$ of the system and finally calculated the mean activity coefficient of $CsNO_3$ $(\gamma_{\pm CsNO3})$ in the mixed system, water activity $(a_w)$, permeability coefficient $(\Phi)$ and excess Gibbs free energy $(G^E)$. This study provided basic thermodynamic data for the separation and extraction of cesium salts.