11th International Heat Flow Calorimetry Symposium on Energetic Materials (HFCS-EM)

Symposium co-chairs

Dr. Manfred A. Bohn and Moritz Heil

List of abstracts

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29 Contributions

The order in this list corresponds not to the order in the presentation schedule

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Venue

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Blank determination in heat flow calorimetry

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A blank determination is an analysis of a sample without the analyte, or an analysis without a sample, thereby going through all steps of the analytical procedure. Whereas in analytical chemistry, regularly performing blank determinations is a basic procedure in order to avoid systematic errors / biased results, the necessity of blank determination has not yet been realized by the Heat Flow Calorimetry community.
Nitrochemie Wimmis has determined the blank value of different ampoule types over the STANAG 4582 sequence of 10.6 days at 80 °C. It turned out that steel ampoules (with and without glass insert) have a very small blank value (heat flow values during entire sequence between −0.2 µW and +0.5 µW; typical total evolved heat in 10.6 days at 80 °C between 0.0 J and 0.3 J). These values are well within measurement uncertainty of the instrument and do not significantly bias obtained results.

The blank measurements of glass ampoules (with caps), however, revealed a significant endothermal reaction in the first few days of the HFC sequence causing significantly negative blank values before finally approaching the baseline; this alters the HFC signal approx. by –3.5 µW after 1 day, by –1.0 µW after 3 days, and still by –0.3 µW after 5 days at 80 °C. Typical blank value of total heat over the entire 10.6 days at 80 °C was found to be approx. −1 J. This bias can be regarded as being acceptable for STANAG 4582 stability assessment of propellants (fully filled ampoules = approx. 3 g sample; "intermediate" heat flow of typically 10–100 µW/g). When measuring small amounts of samples and/or materials with very low heat production (e.g. pyrotechnics, secondary explosives, inert contact materials for compatibility testing), heat flow curves might be well dominated by the blank value of the ampoule – in such cases, the curves need to be corrected by the blank value.

Cause of the endothermal reaction of the glass ampoules has been examined and other possible measures to prevent biased HFC results (e.g. pre-heating of the ampoules) will be discussed.

A simple question with complex answers - is nitroglycerine compatible with boron potassium nitrate or not?

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It was previously thought that the incompatibility reactions between a nitrate ester based propellant and a material known as SR44, which is a simple mixture of boron and potassium nitrate, was due to the oxidation and hydrolysis products of boron causing decomposition of the nitrate esters such as nitroglycerine [1]. In order to investigate the specific reactions of nitroglycerine with boron potassium nitrate (BPN) some additional experiments have been conducted using accelerating rate calorimetry (ARC), heat flow calorimetry (HFC) and differential scanning calorimetry (DSC). It should be noted that BPN is the US equivalent of SR44 but in addition to boron and potassium nitrate, it also contains a polyester- based binder.

The HFC experiments have involved heating NG and BPN in close proximity to each other whereas in DSC and ARC, the two components were in direct contact with each other. Following the HFC experiments, the NG was subjected to high performance liquid chromatography and liquid chromatography / mass spectrometry to determine the concentration of NG remaining and if any NG degradation products had formed.

Despite testing five replicates of samples under each condition the results were complicated by a surprising variability in the data. Further investigations revealed that the BPN pellets were contaminated with magnesium. This was established using atomic absorption spectroscopy and it is known that one of the common contaminants of boron is magnesium. Also, even though the NG was all from the same batch, there might have been slight differences in the residual acid and water content in this liquid.

Additionally, the data revealed that ascertaining the compatibility of two materials is not always clear cut, as in the case of NG and BPN, it was not always unequivocal if NG was incompatible with BPN or not. As a result, some of the issues surrounding compatibility testing of energetic materials using thermal analysis techniques as described in STANAG 4147 [2] and the draft version of AOP-4147 [3] will be discussed in more detail.

References

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Effect of peculiarities of DSC experiment on correctness of the kinetics created

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Influence of certain experimental factors and methods of data processing on the correctness of the resultant kinetics is considered on the basis of dynamic model of DSC.

Firstly, essential effect of sample temperature deviation from linearity or from constant outer temperature due to heat accumulation in the sample on reaction proceeding is discussed. Disregard of this effect may and will be one of the reasons of obtaining the inadequate kinetics. The method for calculation of temperature deviation (reconstruction of sample temperature) is proposed.

Secondly, influence of a DSC curve distortion due to thermal inertia of the cell on the results of kinetic analysis is considered. The method for correction of this distortion (data deconvolution) is presented which can be safely used for processing of data of kinetic experiments. Special attention is paid to the importance of data deconvolution when the kinetic experiment is carried out under isoperibolic conditions.

Finally, the combined effect of temperature deviation and inertia-induced distortions is considered. It should be specifically emphasized that the matters under consideration are especially important when energetic materials are tested due to big heat release and rate of heat generation. At first, all the matters are discussed on the basis of simulated data. This allows elimination of various uncertainties of real experiment and effect of unknown kinetic model and gives vivid illustration of the subject. Then the effects are demonstrated on the basis of experimental data.

Applying adiabatic calorimetry for study of energetic materials - is it possible?

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Nowadays the use of adiabatic calorimetry for study of energetic materials becomes quite popular. It is not surprising considering that testing of these materials under extreme conditions can give valuable information. Unfortunately, the correctness of such experiments is more than questionable.

The origin is simple - energetic materials can generate huge amount of energy which doesn't allow applying sample masses that adiabatic calorimeters were designed for because temperature rise would be well above the permissible limits of the instruments. To avoid this problem one has to use very small samples - often dozens of milligrams instead of typical 3-6 grams (figures are given for the ARC instrument). With such small samples the effective thermal inertia of a calorimetric bomb becomes very big (more than 10-20) and temperature rise becomes acceptable. This method gives rise to serious problems:

- the main principle of adiabatic calorimetry, that is thermal equilibrium between the bomb and the sample, is violated;
- temperature profile in the sample even in very small one becomes essentially non- uniform;
- the thermal inertia (phi-factor) cannot be considered as the constant, it is quite the contrary, phi varies significantly in the course of a reaction.

These and some other related problems that impede application of adiabatic calorimetry are the subject of discussion.

Kinetics-based simulation of thermal explosion - some examples of experimental validation

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Advantages of kinetics-based simulation as the method for analysis of reactive hazards are acknowledged. It is the most universal and in many cases the only method applicable for hazard analysis. It specifically concerns simulation of thermal explosion when large-scale experiments are very expensive if at all possible. Nevertheless, one can often meet certain disbelief in reliability of simulation results. No doubt there are serious reasons for such a disbelief because kinetics is evaluated from experimental data for very small samples (several milligrams in DSC experiments), the simplified physical models are used for explosion simulation, and simulation comes to quite faraway extrapolation.

That is why every case when simulation results can be validated by experiment is important for strengthening of the confidence in simulation. As the examples of this kind are still rare it seemed to be of interest to collect and present some existing ones which is the aim of the presentation. The examples are mostly based on the authors' own results or the results of the users of CISP TSS software.

Heat flow calorimetry and NSWC Crane

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Naval Surface Warfare Center Crane Division has been using heat flow calorimetry to evaluate energetic materials for over twenty-five years and building custom calorimeters for unique testing situations since 1997. Currently NSWC Crane operates approximately $2 million in heat flow calorimeters. This investment in equipment allows for a wide range of capabilities from rapid screening of a batch of test samples (up to 48 in one machine), a mercury free Vacuum Thermal Stability (VTS) option that allows heat and gas measurement, even elaborate heat flow measurements of a 10-pound silver zinc battery under programed charge and discharge cycles, and destructive overcharge testing of lithium cells.

The vast majority of these instruments are custom designed and maintained here at NSWC Crane by our calorimetry team. The instrument support capabilities have branched out to include additive manufacturing of critical instrument components and prototype parts. Over that time the scientists at NSWC Crane have generated three awarded patents, many related invention disclosures and numerous presentations and technical papers on the subject of heat flow calorimetry. It is this experience that allows for the NSWC Crane Calorimetry Science team to create custom calorimeters for various unique situations. This allows for the testing of prototype samples as small as 25mg, small production representative blends or pressed pellets in the gram scale, and even All Up Rounds from the production line containing hundreds of grams of energetic material and weighing several pounds.

Keywords: calorimetry, heat flow, energetic

Heat flow calorimetry of 70mm double base solid rocket motor

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The service and storage lifetime of a double base solid rocket motor was requalified through the use of heat flow calorimetry of the all up motor. The motor is a small diameter system of approximately 70mm diameter, below the indicated maximum diameter of application for STANAG 4582. The motors are used to pull a series of high explosive charges away from the user, detonate at or on the surface of the ground in front of the user thus clearing a way of safe passage. The motors and assemblage were disconnected from the high explosive charges for this testing. The solid motor composition was of a traditional double based propellant. There were only a few assets available for testing so testing the items in their original configuration to enable function testing after calorimetry testing was highly desired. The rocket motor and associated assemblage was first modeled in computer drafting software and printed via additive manufacturing to aid in calorimeter fixture design and selection. The additively manufactured prototype indicated the total displaced volume of the sample was now greater and an additional cell modification would be needed. A modification to a previous cell with fixed reference was completed to enable heat flow calorimetry of the intact rocket motor and assemblage. The samples tested suggest that the manufacturing lots of concern are safe for future storage and testing for performance. The sample motors did show a tendency to outgas and form a mild positive pressure inside the motor casing. This was evident through changes in the heat flow and by visible swelling of flexible seals in the ignition pathway of the motor. The aged motors were then attached to the tow cables and function testing with varying results.

Keywords: Heat Flow Calorimetry, Solid Rocket Motor

Round robin testing of multiple heat flow calorimeter types

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Validation and verification between laboratory sites and equipment types is important for all scientific testing. Through previous HFCS-EM there have been several discussions regarding the observed signal and calibration differences between different manufacturers and generations of heat flow calorimeters. NSWC Crane is well positioned to review the scenario with our colleagues over multiple types and generations of calorimeters. This short study is a fact finding to determine the response of various calorimeters to trials of controlled electrical calibration from an external source and from a chemical reaction. The systems tested will include an unmodified TAM 2277, TAM 2277 with modified data acquisition system, two generations of TAM III units, TAM IV, µIC, and several custom calorimeters designed at NSWC Crane. The initial goal of the study is to assess and quantify the differences (if any) in signal amongst these units and among different site locations where possible. The observations will be made before and after internal calibration for systems equipped with such capability.

Keywords: Heat Flow Calorimeter, Calibration, Round Robin

Heat flow calorimetry: Innovations for test and evaluation of high energy systems

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The continually increasing demands for complimentary operation of systems, along with the perpetual requirement to extend the service life of new and existing systems highlights the need for test and evaluation capabilities equipped to evaluate as many of the common characteristics as possible among the vast array of components of any warfighter support system. This paper describes some of the innovations being applied in the field of heat flow calorimetry to support performance, life cycle sustainability, and failure characterization of several specialized high energy systems using a broadly applicable test system.

High energy systems that use a chemical storage mechanism all have several common concerns that reach beyond their specific design application and are often a point of contention when considering performance, lifecycle, and failure concerns of their own and interacting systems. Most frequently, these concerns manifest as performance, total life cycle or performance after environmental or age-related stress, and of course, failure or premature activation. Each system attempts to quantify these concerns in their own specific field of application. However, a source of commonality will be required to effectively evaluate these concerns when they are incorporated into larger systems of and of system complexes. Heat flow calorimetry has long been used to evaluate safety, stability, and aid in determining performance criteria of propellant, explosive, and pyrotechnic materials. With the advent of several innovations at NSWC Crane, this technique can now be applied across high energy systems. This is made possible by the highly sensitive and nearly universal applicability of this type of thermal analysis.

Keywords: Heat Flow Calorimetry Applications

Modification of TAM III to support multiple test operations – STANAG 4147

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Organizations are routinely asked to generate more data with less resources. Described herein are the efforts conducted to modify a TAM III to perform both Heat Flow Calorimetry (Test 5) and Vacuum Thermal Stability (Test 1 Method 2). This presentation will provide a brief overview of both test methods, some example test systems, and the adaptation of this to TAM III system. The modifications focus on allowing regular and repeatable introduction of a reference gas into the pressure monitoring system offered by TA Instruments. The engineering modifications are discussed necessary to adapt the system to allow for calibration of the internal volume in compliance with the pressure transducer method for vacuum thermal stability testing. Additionally, these modifications also allow for the collection of the evolved gases at test completion or periodically during test for further analysis by a series of further analyses. Included in the paper are representative data for common materials tested by the combined and individual test methods.

Keywords: Heat Flow Calorimetry, STANAG 4147, Hyphenated Techniques

Selection of the correct experimental conditions. Method for kinetics analysis and predictions.

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For kinetic analysis, prediction and simulation it is very important to select the correct conditions for experiment and the correct kinetic method. The selected temperature conditions very often lead to situation where the experimental data do not contain those effects which are most important for the simulation. For example, if the experiment contains only data about decomposition from the liquid phase, then the kinetic model created for these data may be used only for liquid phase. Such model cannot be used reliably for the decomposition in solid phase because the solid decomposition mechanism could be totally different.

Another important condition: correct selection of the experimental heating rate. Total kinetics mechanism of the process at the isothermal conditions could be significantly different from the process kinetics during heating. For example, often the mixture of independent materials has independent decomposition reactions. The sequence and weighting of these individual reactions can be different for heating and for isothermal conditions. Therefore, the heating experiments very often have not enough information to clearly define the behavior of this chemical system at the isothermal condition.

However, even with the correct experimental conditions, the result of kinetic analysis could be incorrect, if the wrong kinetic method was used. It is known, that the model free analysis can analyze only stages of the same energetic direction: either exothermal or endothermal, but not both. Therefore, if the process contains reaction steps with different energetic direction like both exothermal and endothermal, then model-free analysis is not applicable, produces incorrect results and cannot ensure reliable predictions and simulations. Another example with a high probability of using the incorrect method is the process with competitive reaction steps where reaction products and consequently energetic effects of the process depend on the heating rate. In this case the reaction mechanism strongly depends on the heating rate and we must be very carefully in the selection of the kinetic analysis method.

Current work contains also examples of correct and useful kinetics methods: from model free to model based with consecutive, competitive or independent reaction steps. The main rules for selection of the correct kinetic method are formulated. The software NETZSCH Kinetics Neo is used as the main tool of analysis having different kinetic methods.

Keywords: Kinetic analysis, model free analysis, kinetic model, kinetic predictions

Continuous monitoring of shelf lives of materials by application of data loggers with implemented kinetic parameters

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A procedure is presented in which a track and trace system enables the continuous evaluation of the shelf life (expiry date) of perishable goods. It can help in the optimal storage/shipment and results in significant decrease of waste. The evaluation of the shelf life of e.g. energetic materials, food, pharmaceutical materials, polymers at room- or daily climate fluctuation temperatures requires the kinetic analysis at the temperature range, which is as much as possible similar to those at which the products will be stored or transported. The collection of the data at these relatively low temperatures is time and effort consuming. Therefore, only a limited number of experimental points is generally used for the evaluation of the deterioration rate. Kinetic analysis of such sparse points requires advanced kinetic analysis based for example on Akaike and Bayesian information criteria [1].

We compare the results of the evaluation of the shelf life of propellant and vaccine calculated by advanced kinetics and simplified *0-th* and *1-st* order kinetic models. The obtained simulations show that the application of simplified kinetics or commonly used the Mean Kinetic Temperature approach may result in an imprecise estimation of the shelf life. The implementation of the kinetic parameters obtained from advanced kinetic analysis into programmable data loggers allows us, in contrast to existing solutions which only monitor the temperature, the continuous, online evaluation and the display on the smartphone of the actual extent of the deterioration of materials. The proposed approach is universal and can be used for any goods, any methods of shelf life determination and any type of data loggers.

Keywords: shelf life, data loggers, internet of things, advanced kinetic analysis, propellants, vaccines.

References

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Thermal behaviour of quasi-autocatalytically decomposing solids: How phase transitions, melting and sample mass can influence the experimental workflow

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During the determination of thermal behavior of solids based on kinetic analysis, one has to take into account the correct temperature and reaction extent at which kinetic data are collected and calculated. If phenomena such as a polymorphic transformation and/or melting do not precede the decomposition, then the experimental window (the range of heating rates or temperatures) can be optimized relatively easily. However, in the case where the phase transition occurs very close to the beginning of the decomposition, the collection of the data required for the proper kinetic analysis may be very difficult. Such compounds belong to the solids of the quasi-autocatalytic decomposition type. It seems obvious that the kinetics of the decomposition must be investigated for this phase which is stable at ambient temperatures during the long-term storage. This issue can be well illustrated by the simulations of the Self Accelerating Decomposition Temperature (SADT) value of the azo-bis-isobutyronitrile (AIBN). The kinetic parameters required in simulation workflow were obtained from heat flow calorimetry experiments performed at temperatures of the stability range of low-temperature (L-T) polymorph of AIBN. Thermal Activity Monitor (TAM^{TM}) data were collected in the range of 55-70°C. Having kinetic parameters of the reaction and the heat balance of the system it was possible to predict the rate of the decomposition of the material under any, arbitrarily chosen temperature mode for any sample size. The presented simulations illustrate the scenario of the progressive increase of the sample mass from 1 mg up to 50 kg. When sample mass increases, the heat generated during decomposition progressively exceeds the rate of the heat transfer. The resulting heat accumulation leads to self-heating of the sample and creation of a temperature gradient inside the material. The simulated SADT value for L-T AIBN amounts to 46°C. This is very similar to the computed results obtained in the BAM project [1,2] for the high-temperature (H-T) form of AIBN which amounts to 47°C and is also in full agreement with the large scale experimentally found SADT of L-T AIBN (47°C) [1]). The prerequisites for collecting proper kinetic data for the quasi-AC type energetic materials in which the phase change phenomena (polymorphic transformation or melting) precedes the decomposition are discussed. The apparent paradox when the application of incorrect kinetics applied in narrow □□or *T* ranges may sometimes result in the correct predictions of some safety parameters, such as SADT, is discussed and explained.

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New accessories and tools for TAM

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Many samples will evolve gases during decomposition. Pressure building inside a closed ampoule can cause expansion of the cap and result in a disposable glass ampoule getting stuck in the calorimeter. To avoid this happening a new pressure release lifter is introduced. This pressure release lifter is a special ampoule lifter for 3 and 4 mL disposable glass ampoules that will vent excess pressure outside the calorimeter. This lifter can be set to vent at pressures between 1-3 bar. If higher pressures from the measured samples are expected the vacuum/pressure ampoules are recommended. This will hold a pressure up to 10 bar before release.

Another safety feature introduced in the software is an emergency cool function. This emergency cool function can be set to execute once a sample reach a certain predefined heat evolution. There will be an option to stop the execution by removing the critical sample.

TAM Assistant does have a wizard and evaluation program for STANAG 4582, but currently not for STANAG 4147. A short information will be given on how to use TAM Assistant to evaluate compatibility according to STANAG 4147.

An Investigation into PETN Acidity using Heat Flow Calorimetry

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Abstract

Pentaerythritol Tetranitrate (PETN) is an organic nitrate ester primarily used as the filling in blasting caps, booster formulations and detonators for both commercial and military applications. It is known that the appropriate functioning of the device is related to the PETN properties hence degradation will impact on the functioning of the device. As PETN decomposes hydrolysis can result in acidity increase, further shortening the life of the explosive and devices containing the explosive.

An initial study PETN decomposition using heat flow calorimetry has previously been presented[1]. This work has developed to investigate the thermal response of PETN samples of different ages exhibiting varying levels of acidity, including samples withdrawn from service returns. Correlations will be made between starting acidity and time to a given thermal response, enabling relative decomposition rates at near operational temperatures to be predicted from material acid content.

Keywords: Heat Flow Calorimetry, PETN; Acidity

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Use of Calorimetric Techniques with High Explosives

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Abstract

The National Regulatory Authority requires that all explosives used in munitions are chemically assessed against other substances used in manufacture, assembly or storage of those munitions to ensure no detrimental effects occur. Traditionally a vacuum stability method has been used however, recent changes provide potential to adopt thermo-analytical methodologies including Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA), Heat Flow Calorimetry (HFC) and Accelerating Rate Calorimetry (ARC) to assess chemical compatibility of explosives.

Although the ability to use alternative or combinations of techniques provides a more versatile approach to compatibility testing; it is crucial that the tests are evaluated and found to be suitable before they can be adopted. The applicability of these techniques to high explosives has not been fully validated.

A suite of materials have been tested using the techniques listed to provide a comprehensive evaluation of their suitability for assessment of high explosives. Standard DSC and TGA decomposition experiments were carried out alongside modulated DSC to monitor changes to the heat capacity of the explosives in the presence of adulterants. HFC experiments at 80 °C were carried out to provide a lower temperature test environment in comparison. ARC experiments were undertaken to investigate the materials interaction influences on thermal safety parameters.

The results indicate that explosives with good thermal stability and thus high decomposition temperatures do not lend themselves well to DSC and TGA decomposition experiments. Standard decomposition test sentencing is not applicable when adulterant materials undergo high temperature thermal transitions prior to any reaction with the explosive. It is recommended that tests are carried out at temperatures more representative of use and a sentencing criteria developed to reflect this. Measurement of changes to heat capacity shows promising results. HFC and vacuum stability results have been compared alongside DSC and TGA. Observations from ARC experiments have been used to propose an initial sentencing criteria.

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

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Abstract

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 IR 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 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 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 species (carbonates, hydrogen carbonates and carboxylates) introduced when carbon dioxide reacts with ceria surfaces.

It is concluded that HFC can provide reasonable data related to the aliquot size of the CO_2 added, however data quality is not ideal with options discussed for improvements through consideration of the oxide loading.

Keywords: Heat Flow Calorimetry, Adsorption, Carbon Dioxide, Ceria, Infra-Red Spectroscopy

Ultra-high sensitivity ARC testing – a link to isothermal STANAG 4582 testing.

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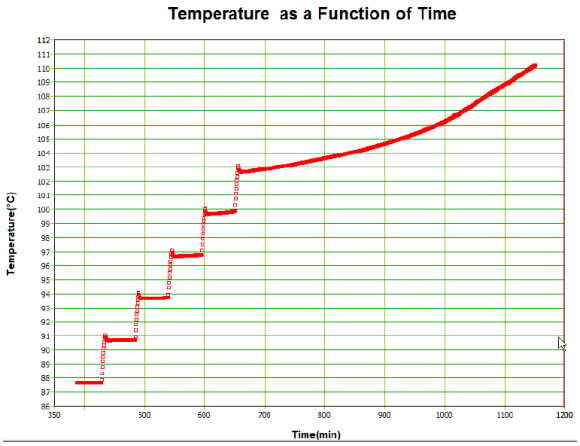
Dependent upon ageing conditions NATO STANAG 4582 testing takes significant time from a few days (90°C) to several months (60°C). the tests tie up valuable instrumentation and need quality personnel. This contribution illustrates the potential of the Accelerating Rate Calorimeter (ARC[tm]) to gain information on propellant stability, in testing at a sensitivity much higher than usual. The aim is to use ARC as a precursor to isothermal testing, with a view to reduce significantly the testing required. The ARC and its applications to energetic materials are well known. There are very many applications well reviewed by Bohn and Pontius (1). Due to energy release a small sample mass is used. Bunyan reported testing with larger sample mass of energetic materials (2). Robust and versatile the ARC is also a technique available in many laboratories. A large mass may be used if the experiment is curtailed prior to serious self-heating.

In this presentation an ARC study of smokeless (rifle) powders PyrodexP, H414 and IMR 4895 will be described. Results of ARC tests are shown where conditions are chosen to maximize sensitivity and therefore determine onset at minimal heat release – at the lowest temperature. The protocol being 1°C heat steps, long wait time and then detection of exotherm from 0.001°C/min or 0.002°C/min. A lightweight holder and a sample mass of near 6 grams is chosen. Testing focusses in the temperature range 75 to 95°C. The ARC needs to be well 'calibrated' to have such isothermal stability, but this is possible. The test takes 1 day. Detection of heat flow is thus close to 50 µW/g. The ARC was not developed to have high sensitivity and testing under adiabatic conditions cannot match the sensitivity of the best isothermal calorimeters. However, results indicate the potential for ARC testing as a precursor to isothermal calorimetry according to STANAG 4582 testing and ARC can contribute reducing the testing needed and shortening the time required, as illustrated below.

1. Bohn and Pontius Proc. 43rd Int. Annual Conf. of ICT, Paper 57, Karlsruhe, Germany, June 2012
2. Bunyan et al Proc. 31st Int. Annual Conf. of ICT, Paper V4, Karlsruhe, Germany, June 2000

Time (min)	Temperature (°C)	Temp Rate (°C/min)
95.491000	69.653000	-0.000000
151.492000	72.709000	-0.000000
206.992000	75.697000	0.000000
262.492000	78.689000	-0.000000
317.992000	81.687000	-0.000000
373.492000	84.713000	0.000000
428.492000	87.668000	0.000000
483.993000	90.706000	0.001000
539.493000	93.723000	0.001000
594.993000	96.776000	0.002000
650.493000	99.903000	0.004000
700.493000	102.875000	0.007000



HFC studies of conventional and novel energetic materials

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Heat Flow Calorimetry (HFC) has been used (NATO 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 or 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 TAM^{TM} IV from company TA Instruments 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 behavior of heat flow as the samples are artificially aged.

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

Keywords: HFC, propellants

Slow cook-off modeling for medium caliber ammunition

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The U.S. Army CCDC Armaments Center at Picatinny Arsenal, NJ is working to improve the responses of various medium caliber ammunition items when subjected to the NATO Insensitive Munitions (IM) Slow Cook-off (SCO) test. As per NATO STANAG 4382 Ed. 2, this test subjects the item to a gradually increasing ambient temperature, which for example might be produced by a fire in an adjacent munition store. One technique which has been successful in addressing SCO for these items is warhead venting, in which the cartridge is designed to release the fuze assembly from the warhead before thermal explosion occurs. This allows energetic decomposition products to escape thus avoiding pressurization of the explosive charge and resulting in a nonviolent burning reaction. Some explosives commonly used in U.S. medium caliber ammunition are PBXN-5 (95% HMX, 5% Viton) and Composition A5 (99% RDX, 1% Wax). Simple models for energetic self-heating based on zero-order Arrhenius kinetics can be obtained from Differential Scanning Calorimetry (DSC) using, for instance, the Flynn/Wall/Ozawa method [1], and can sometimes predict the time and location of ignition. However in the design of warhead vent features, it is useful to be able to model the pressures resulting from the evolution of gaseous products and their effect on self-heating in sealed and vented systems. Hobbs, et al. have previously developed a cook-off model for the plastic bonded explosive PBX 9501 (95% HMX, 2.5% Estane, 2.5% BDNPA/F) which provides this capability [2]. The model utilizes a pressure dependent five-step mechanism parameterized using Sandia Instrumented Thermal Ignition (SITI) experiments. Hobbs determined that the PBX 9501 model can be used to predict cook-off of other plastic bonded explosives containing HMX and an inert binder, such as LX-10-0 (95% HMX and 5% Viton) [3]. This is achieved by accounting for the correct amount of HMX in the explosive and limiting the nitroplasticizer reaction. A similar model has also been developed for RDX. In this work, modeling predictions obtained with the finite element code SIERRA ARIA are compared with SCO data for several medium caliber ammunition items.

Keywords: Insensitive Munitions; Explosives; Cook-off; Venting; Modeling

References:

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[2] M. L. Hobbs, M. J. Kaneshige and W. W. Erikson, "Modeling the measured effect of a nitroplasticizer (BDNPA/F) on cook-off of a plastic bonded explosive (PBX 9501)," Combustion and Flame, vol. 173, pp. 132-150, 2016.
[3] M. L. Hobbs. “Modeling Cook-off of HMX Based PBX Explosives with Inert Binders”. Private Communication, February 13, 2017.

Controlled thermal test on high explosive cylinders

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The study of non-nominal initiation of high explosives is essential to assess munition safety. Several aggressions have to be considered, among them low or intense impact, and fast or slow cook off. The number of aggressions and the lack of comprehension on the explosive behavior make the experiments and modeling complex.
We propose a study of controlled thermal test on high explosive cylinders leading to combustion or deflagration. Unlike fast or slow cook-off, the heating conditioning is specially chosen so as to ignite a reaction at the center of the explosive bar. A slow controlled temperature rise is assigned to the cylinder surface in order to bring all the volume to an isothermal value, which is kept until a reaction appears at the center. This controlled thermal test is among the hardest to treat in pyrotechnic safety because of auto-confinement due to the initiation at the heart of the explosive cylinder. Our study is based on an up-scaling procedure, leading thermal experiments and modeling at the same time.
On a small-scale level, a “model-free” kinetic for a given explosive is extracted from DSC experiments, involving a few milligrams of energetic material, thanks to the AKTS program. This kind of “model-free” kinetic provides two parameters of an Arrhenius law, pre-exponential factor Z and activation energy E_a both reaction rate dependent, and chemical energy Q, that can be easily introduced in prediction models. Middle-scale experiments are driven to validate this kinetic. An unconfined *quasi* 1D-cylindric 500 g bar of high explosive is thermally packed and instrumented in order to monitor temperature at different points. The isothermal temperature is selected to enable a reaction during a day work experiment. The temperature is tightly controlled during the experiment to prevent the risk of initiating the reaction at the surface, which is closer from a fast cook-off than a slow one. Then controlled thermal tests of confined explosive cylinder are led. They show that a deflagration can occur in accidentals conditions. Prediction is again carried out with AKTS Thermal Safety module. The program uses the “free-model” kinetic as input parameter and takes the casing thermal properties into account. The comparison between the reaction delay given by experiment and calculation are good for unconfined samples and are quite good though less accurate in the confined case.

Keywords: Kinetic, modelling, prediction, AKTS, deflagration

CEA-DAM:
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A way to improve the safe use of closed stainless-steel ampoules in heat flow microcalorimeters (HFMC)

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Increasingly the traditional glass ampoules with butyl rubber sealing and crimp lid are replaced by tightly closed stainless steel ampoules in measurements with HFMC. The glass ampoules are easy to handle and the provide a basic safety aspect, in that with pressure built-up the lid bends up. By piercing the lead after measurement, the lid contracts mostly in such a way that the ampoule can be drawn out of the measurement channel. But sometimes this fails, and the calorimeter channel is contaminated. This happens 'regularly' when pressure built-up is more than 2 to 3 bars. To circumvent these problems, one can use the 4 ml stainless-steel ampoules or even Hastelloy ampoules. The pressure resistance is much higher and mainly limited by the forces which the thread of the caps can hold. As recommendation: one should not use ampoules with the viton or rubber sealing and circlip or retaining ring fixture of the lid. The opening may cause an uncontrolled troughing of the lid by the sudden pressure release. This happens not with the thread caps, because already after a half opening turn the pressured gas is safely released and the lid is still held by the thread. If one encounters a pressure built-up beyond the tightening force the cap thread can provide, the lid is lifted a bit and gas is released. But surely this functions only then as a 'built-in' safety effect, when the pressure built-up or the gas generation of the sample is slow enough that the inertia of the ampoule lid has time to open.

The question is now, how much gas can be produced by the sample and what can be the pressure built-up in the ampoule. To be on the safe side one may assume a total decomposition of the sample and the amount of gas should not exceed the pressure tightness of the ampoule. Another way is to observe the conversion via the generated heat Q and calculate the corresponding gas formation and resulting pressure in the free volume of the ampoule. This paper describes the procedure to achieve a fairly safe assessment of pressure built-up in stainless-steel ampoules. To determine the gas amount the sample can produce the thermodynamic controlled decomposition of the sample is considered. A method to get such data is for example the ICT Thermodynamic Code. During presentation it will be shown how this program system can be used for this objective.

Keywords: heat flow microcalorimetry, stainless steel ampoules, pressure built-up, safe use

Kinetics of thermo-chemical decomposition of RDX in cyclohexanone and gamma-butyrolactone determined with ARC™ and heat flow microcalorimetry

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To improve its crystalline quality RDX is processed in suitable solvents, among them are cyclohexanone and gamma-butyrolactone. In spite of its relatively high thermal stability RDX can decompose to a certain extend during processing. Several qualities of RDX were investigated: so-called insensitive RDX (I-RDX) from Eurenco, Sorgue, France and so-called sensitivity reduced RDX (S-RDX) from Chemring, Saetre, Norway. In addition, both types were used in a coarse (class 1) and a fine (class 5) particle size.

With ARC™ (Accelerating Rate Calorimetry) solutions between 6 mass-% and 10 mass-% of RDX in the two solvents have been used with 1 inch titanium ARC™ bombs. The used instrument was so-called ES-ARC from THT Inc. Bletchley, MK1 1SW, UK. It was operated in the so-called 'heat-wait-search' mode to register the decomposition exotherm reached by pseudo-adiabatic selfheating. The temperature range of detected decomposition is between 130°C and 230°C. The amount of RDX was used-up during the course of the full decomposition curve, means after the end of selfheating all RDX was consumed. The curves show an initial faster increase in self-heat rate. Mostly this is indicative for chemical species which accelerate decomposition. Such features can be caused autocatalytically or by impurities. The curves were described with reaction kinetic models and Arrhenius parameters have been obtained.

The heat flow microcalorimetry (HFMC) measurements were performed with TAM™ III and a modified TAM™ II instruments from TA Instruments. Isothermal measurement temperatures were 90°C, 100°C, 110°C and 120°C. Because of the relatively high measurement temperatures with HFMC, one can combine the results of both measurement methods, which is tried in this paper.

To have an indication about the amount of RDX decomposition in the HFMC runs the solution were analysed with HPLC to find out the residual RDX content in the solutions.

Keywords: ARC, heat flow microcalorimetry, RDX, solution in cyclohexanone, solution in gamma-butyrolactone, kinetic evaluation

Assessment of ageing state of several double base rocket propellants with mass loss, stabilizer consumption and heat flow microcalorimetry

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The assessment of the ageing state, rate present rate of ageing and the perspective of residual or further safe storage and use times is an important task to guarantee a controlled and accountable behaviour of nitrate ester based propellants as double base (DB) rocket propellants (RP) and nearly all types of gun propellants presently in service.

At ICT recently several DB-RP have been investigated on the ageing state with heat flow microcalorimetry (HFMC), mass loss (ML) and stabilizer consumption according to the so-called single temperature method of the AOP-48 (NATO Allied Ordnance Publication). The age of the propellants at time of investigation was between 2 and 18 years. Especially the propellant with 18 years age was feared to be unsafe already. All three methods give congruent assessment data. The result is that all propellants are still safe to use and have a further safe in-service time of 10 years according to AOP-48 and NATO STANAG 4582 (named also Heat Flow Microcalorimetry STANAG).

It turned out that the heat flows of the DB-RP are still low, far below the limit values set by STANAG 4582. This gives the possibility to extend the predicted time of safe use of more than 10 years. It will be shown how this can be achieved with HFMC and ML data.

Further investigation methods as gas generation, adiabatic selfheating and molar mass decrease were applied also to assure the assessments.

Keywords: double base rocket propellants, ageing state, assessment of safe use time, heat flow microcalorimetry, mass loss, AOP-48, STANAG 4582

Evaluation of the high temperature ageing of a solid gas generant by mass loss and heat flow microcalorimetry

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A high temperature gas generant (GG) is investigated at temperatures between 75°C and 120°C with heat flow microcalorimetry (HFMC) and mass loss (ML). The GG is supposed to work in high temperature environment (> 60°C) for several years and even up to decades. This time-temperature load is far off from the standard operating temperatures and time ranges in military use and even from automotive use. It is a challenge to find out the behavior of such GG, since the ageing temperatures must be in the same range as the planned operating temperature.

To avoid unnecessary risks for calorimetric equipment, high temperature mass loss is used as a first assessment technique. Based on these results, HFMC is conducted. In this work, it is mainly the objective to evaluate how both techniques can work together.

Calculation of the activation energy is performed by using reaction models and iso-conversional (Friedman and integral) methods for both measurement techniques. Iso-conversional methods are usually not possible for mass loss measurements due to insufficient data points to calculate conversion-dependent activation energy. The interpolation of those missing values is also called imputation (not just interpolation) in data handling statistics, and there is a large number of different approaches, from model-based fitting to simple linear regression between data points. Selected techniques will be presented and evaluated.

Heat flow microcalorimetry data serves then as the backbone of the assessment of different algorithms for imputing the missing mass loss data. High quality data and careful analysis are necessary to get reliable results. A comparison between the calorimetric data and the mass loss data aims to show how the differences and similarities of both methods affect the results.

Keywords: heat flow microcalorimetry, mass loss, kinetics, Friedman iso-conversional method

Defining the UK methodology for the stability testing of energetic materials

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The UK Defence Ordnance Safety Group (DOSG) provides advice to project teams, the armed forces and industry on Ordnance, Munitions and Explosives (OME). The UK needs to maintain research into new energetic material technology. As the UK's inventory is increasingly procured from non UK sources, it has become essential to understand testing and evaluation undertaken in the country of manufacture. It is vital to align UK testing with that of other NATO allies, whilst maintaining the UK database of knowledge to ensure continued OME safety.

Current UK stability testing of propellants consists of the Abel Heat Test, the 80°C Self Heating Test, the Vacuum Stability Test and single temperature stabiliser depletion in accordance with AOP48 Ed.2. However, the supply chain of propellants to the UK has changed and will continue to vary in the future. As a result, the UK service does not always have access to sufficient characterisation data and no historic data exist to allow assessment of their performance in stability testing.

Consequently, there is a need to confirm the analytical techniques which are appropriate for assessing the stability of energetic materials entering UK service. In order to do this, DOSG are supporting a number of experimental programmes, which aim to define the future UK test methods.

One of these programmes involves using accelerating rate calorimetry, the mass loss test and heat flow calorimetry to understand the stability of a selection of gun propellants. One of the aims of this programme is to define the reproducibility of the techniques and to understand the variability of the results, which have been observed previously for such materials.

This programme is in the very initial stages and so this paper will describe the approach the UK intends to take with respect to stability testing programmes, along with some of the early results. The data from a similar programme using tetryl (a high explosive) will also be discussed to illustrate the advantages of using modern analytical techniques for assessing the stability of energetic materials.

Keywords: accelerating rate calorimetry, heat flow calorimetry, stability, characterisation**.**

Reaction calorimetry in flow reactors - fast reaction screening and process design

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To keep the time to market as short as possible, detailed knowledge about a chemical reaction system must be available in an early phase of process development, facilitating dependable decisions about synthesis strategies and process management. Process analytical techniques, which provide a high level of information while keeping experimentation times short, are essential for of effective process design in chemistry and biochemistry. In this context, the combination of continuous-flow processes with calorimetric measurement techniques offers an approach to fast process design, process diagnostics and process optimization. Calorimetry is an analytical method for investigating thermal effects resulting from chemical reactions and/or changes in physical states. Knowing the heat flows occurring in a chemical reaction system provide crucial information for the successful design and development of new chemical processes as well as for optimizing existing processes. Measurement of heat flows is therefore an attractive methodical approach for developing new and rapid in-process monitoring techniques.

Here we report on the development of various small-volume, continuously operated reaction calorimeters on the basis of flow reactors, which permit rapid screening of thermokinetic key data of chemical reactions. At the heart of the calorimeters are sensor arrays based on Seebeck elements for the localized, quantitative characterization of heat flows. The measurement of the heat flows has the advantage that the heat release rate of the reaction is directly proportional to the reaction rate. This allows easy access to kinetic and thermodynamic data of chemical reactions (heat of reaction, reaction rate and conversion). The reactors themselves may be made of various materials (stainless steel or glass); moreover, they may be exchanged to adapt the most appropriate reactor to the reaction being analyzed, for example in terms of residence time or mixing performance. The combination of continuous-flow technology and efficient heat flow sensors opens the way to rapid and efficient screening of chemical reaction parameters and allows acquisition of safety data. During screening experiments, the influence of individual process parameters (e. g. concentration, stoichiometry, use of alternative reactants, temperature, residence time, etc.) can be followed directly by observing the heat signal – both in a qualitative and quantitative manner. The measurement of the heat flows is in real-time; time-consuming calibrations for the heat transfer are not required. Even targeted investigations and quantitative analysis of the energetic potential of critical process conditions (worst case scenarios) can be conducted safely. The performance and the accuracy of these new devices are demonstrated for different exothermic reactions in the liquid and liquid/liquid regime.

Keywords: continuous micro reaction calorimetry, process optimization, safety analyses

Assessment of aging of two developmental double base propellants with HFC and stabilizer depletion

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Two developmental propellants were formulated as alternatives to an extruded double base type propellant with the goal of improving long-term aging and heat cycling responses. The new propellant formulations seek to improve the service life of a currently fielded propellant. In order to achieve this goal, the two developmental propellants contain a different stabilizer than the currently fielded propellant at differing percentages. The amount of stabilizer in the new formulations was varied to determine the effect on aging, burning rate, and mechanical properties. This work presents correlations between current long-term aging studies, measured by stabilizer depletion over time, with heat flow calorimetry data. Samples aged during the heat flow calorimeter study were also analyzed with HPLC for additional comparisons and correlation.

Keywords: service life extension, propellant formulation, heat flow microcalorimetry, stabilizer depletion

Scale up from Lab to Plant with non-isothermal reactions using Reaction Calorimetry

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Reaction calorimetry is used to identify thermodynamic and kinetic parameters, which are crucial for safety evaluation and design, optimization and scale up of chemical processes. Laboratory-based and production-oriented chemical reactions are essentially performed in the same way; however, safety analyses and risk assessment is not always representative of the exact final process. This can occur especially when the reaction takes place during a temperature ramp. The goal of this presentation is to educate researchers on how to use calorimetry to up-scale chemical reactions in a safe way. For this purpose, examples of isothermal and non-isothermal experiments will be presented and analysed using a family of Reaction Calorimeters.

Non–isothermal experiments are commonly used in production to reduce the risk of a high heat of accumulation and to get a better quality and/or higher yield. The performance and accuracy of the Mettler-Toledo calorimeters are demonstrated on the basis of a number of chemical reactions. The results demonstrate the high precision of the calorimeters and highlight the fact that the equipment can easily deal with fast and highly exothermic reactions under challenging and problematic non-isothermal conditions for scale up purposes.

Keywords: reaction calorimeter, non-isothermal reactions, safety assessment, reaction process design