NATO STANDARDIZATION OFFICE
BUREAU OTAN DE NORMALISATION

11 December 2015

NSO/1573(2015)CASG/4515

STANAG 4515 (Edition 2) – EXPLOSIVES: THERMAL ANALYSIS USING DIFFERENTIAL THERMAL ANALYSIS (DTA), DIFFERENTIAL SCANNING CALORIMETRY (DSC), HEAT FLOW CALORIMETRY (HFC), AND THERMOGRAVIMETRIC ANALYSIS (TGA)

References:

A.   NSA/0817-PCS/4515 dated 23 August 2002
B.   NSA/0673(2013)LMC/4515 dated 30 May 2013

1.   The enclosed NATO Standardization Agreement, which has been ratified by member nations as reflected in the NATO Standardization Document Database (NSDD), is promulgated herewith.

2.   The references listed above are to be destroyed in accordance with local document destruction procedures.

1.   **ACTION BY NATIONAL STAFFS**

3.   National staffs are requested to examine their ratification status of the STANAG and, if they have not already done so, advise the CASG through their national delegation as appropriate of their intention regarding its ratification and implementation

Edvardas MAŽEIKIS
Major General, LTUAF
Director, NATO Standardization Office

Enclosure:
STANAG 4515 (Edition 2)

NATO Standardization Office – Bureau OTAN de normalisation
B-1110 Brussels, Belgium   Internet Site: http://nso.nato.int
e-mail : nso@nso.nato.int – Tel 32.2.707.5556 – Fax 32.2.707.5718

NORTH ATLANTIC TREATY ORGANIZATION
(NATO)

NATO STANDARDIZATION OFFICE
(NSO)

STANDARDIZATION AGREEMENT
(STANAG)

SUBJECT: EXPLOSIVES; THERMAL ANALYSIS USING DIFFERENTIAL THERMAL ANALYSIS (DTA), DIFFERENTIAL SCANNING CALORIMETRY (DSC), HEAT FLOW CALORIMETRY (HFC), AND THERMOGRAVIMETRIC ANALYSIS (TGA)

Promulgated on 11 December 2015

Edvardas MAŽEIKIS
Major General, LTUAF
Director, NATO Standardization Office

RECORD OF AMENDMENTS

No.	Reference/Date of amendment	Date entered	Signature

EXPLANATORY NOTES

AGREEMENT

1.   This STANAG is promulgated by the Director NATO Standardization Office under the authority vested in him by the North Atlantic Council.

2.   No departure may be made from the agreement without informing the tasking authority in the form of a reservation. Nations may propose changes at any time to the tasking authority where they will be processed in the same manner as the original agreement.

3.   Ratifying nations have agreed that national orders, manuals and instructions implementing this STANAG will include a reference to the STANAG number for purposes of identification.

RATIFICATION, IMPLEMENTATION AND RESERVATIONS

4.   Ratification, implementation and reservation details are available on request or through the NSO websites (internet http://nso.nato.int; NATO Secure WAN http://nso.hq.nato.int).

RESTRICTION TO REPRODUCTION

5.   No part of this publication may be reproduced, stored in a retrieval system, used commercially, adapted, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publisher. With the exception of commercial sales, this does not apply to member or partner nations, or NATO commands and bodies.

FEEDBACK

6.   Any comments concerning this publication should be directed to NATO/NSO – Bvd Leopold III - 1110 Brussels - Belgium.

NAVY/ARMY/AIR

NATO STANDARDIZATION AGREEMENT
(STANAG)

EXPLOSIVES: THERMAL ANALYSIS USING DIFFERENTIAL THERMAL ANALYSIS (DTA), DIFFERENTIAL SCANNING CALORIMETRY (DSC), HEAT FLOW CALORIMETRY (HFC) AND THERMOGRAVIMETRIC ANALYSIS (TGA).

Annexes:

A.   Thermal characterization of explosives.

B.   Test Procedures.

C.   Further investigations possible using the techniques described.

D.   Data sheet for reporting of results.

E.   Schematic diagrams of apparatus used for thermal analyses.

F.   Examples of thermal curves.

G.   Reference Materials for Differential Scanning Calorimetry and Differential Thermal Analysis.

Related documents:

1.   ASTM E473- 07a Standard Terminology Relating to Thermal Analysis and Rheology

2.   ASTM E1142 -07 Standard Terminology Relating to Thermophysical Properties

3.   STANAG 4582, "Explosives, Nitrocellulose Based Propellants, Stability Test Procedures and   Requirements Using Heat Flow Calorimetry", 1st Edition, March 2004.

4.   STANAG 4147, "Explosives, Chemical Compatibility of Munition Components with Explosives and Propellants (Non-Nuclear Applications)", 3rd Edition *2008.*

5.   STANAG 4525, "Explosives, Physical/Mechanical Properties, Thermomechanical Analysis for Determining Coefficient of Linear Thermal Expansion (TMA)", 1st Edition 2001.

6.   STANAG 4540, "Explosives, Procedures for Dynamic Mechanical Analysis (DMA) and Determination of Glass Transition Temperature", 1st Edition 2003.

AIM

1. The aim of this agreement is to standardise test procedures for thermal characterization of explosive materials using Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Heat Flow Calorimetry (HFC) and Thermogravimetric Analysis (TGA).

2. This agreement is intended for use by the NATO Participating Nations.

AGREEMENT

3. Participating Nations agree to adopt the test procedures described in Annex B for the characterization of explosives using thermal analytical techniques and to use the data sheet at Annex D for reporting test results.

IMPLEMENTATION OF THE AGREEMENT

4. This STANAG is considered implemented by a nation when that nation has issued instructions that thermal characterization of explosives shall be performed by the test procedures described in this STANAG.

WARNING

5. This STANAG calls for the use of substances and test procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and in no way absolves the user from the statutory obligations relating to health and safety at any stage during use.

THERMAL CHARACTERIZATION OF EXPLOSIVES

1. **INTRODUCTION**

1.1. Information on the thermal characteristics of explosives is important from a safety and operational viewpoint. Characteristics displayed on thermal curves from the major dynamic techniques Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) can be used to monitor samples in comparison to controls, to examine if changes have occurred which may affect stability and consequently safety and operation. Differences due to sample preparation, ageing, packing and geometry may be recognised from thermal data. All these three analytical techniques will be summarized as 'dynamic' techniques although they can also be operated isothermally.

In contrast to these three above mentioned techniques, Heat Flow Calorimetry (HFC) is mainly used isothermally even if some calorimeters can also be used dynamically. Its application to nitrocellulose based propellants has been proven as being very suitable. Due to a considerable higher precision in temperature measuring and much larger samples it is about 1,000,000 times more sensitive than DSC and can thus be operated at considerably lower temperatures. On the other hand, the upper operating temperature of most of these calorimeters is much lower than that of the other three techniques and may not be applicable for energetic materials of high thermal stability. HFC is thought to more closely observe a natural ageing mechanism than do the dynamic techniques at elevated temperatures.

1.2. The major methods used to obtain thermoanalytical data are fairly well established. However, the application of these thermal techniques to the study of explosives requires special considerations due to their mode of operation. Generally, sample size is kept to a minimum for safety reasons since the high rate of energy released on decomposition can lead to "thermal runaway". Instruments are probably unlikely to be able to follow such rapid energy changes and data can be lost or wrongly interpreted as a result. Heating rates are, therefore, carefully chosen to match sample size in order to keep the reactions under control while producing signals with measurable magnitude.

1.3. The primary techniques used to obtain information on thermal properties are DTA, DSC and TGA. Each technique is valuable by itself but additional information may be gained using combined techniques such as DTA/TGA and TGA linked to a Fourier Transform Infrared Spectrometer (FTIR) or to a mass spectrometer (MS) for evolved gas analysis (EGA). DTA studies tend to yield thermal curve shapes comparable to those generated by DSC. DTA is quantitative only for temperature but, unlike DSC, does not quantify heat generation as well. DTA instrumentation, however, is generally more robust and consequently larger samples and higher heating rates can often be used quite safely. The technique is particularly useful for the study of ignition temperatures of pyrotechnics and primary explosives when a photodetector system is used to monitor the "flash" associated with ignition.

1.4. Dynamically gained data cannot normally be used directly for determining the isothermal storage conditions of explosives. For example, the dynamic decomposition temperature depends strongly on experimental conditions. In any case this temperature is much higher than the tolerable temperature of isothermal storage. Extrapolations to ambient temperature may be possible if multi heating rate data are available.

1.5. Isothermal data can be used for kinetic evaluation if (at least) three different temperatures are used, with typically 10°C difference between each two temperatures. A model free isoconversional evaluation for the determination of the activation energy is sufficient for extrapolation to ambient temperature. However, depending on the temperatures used and the decomposition rate of the explosive, this test may be very time-consuming.

2. **GENERALISED THERMAL ANALYSIS SYSTEM**

2.1. The techniques Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Heat Flow Calorimetry (HFC) and Thermogravimetric Analysis (TGA) operate under the same general principles.

2.2. The sample is placed in an environment, the temperature of which is regulated by a temperature programmer. Physical/chemical sample parameters are monitored by an appropriate device that produces an electrical output which is the analogue of the chemical or physical change occurring to the sample. The output is amplified electronically and fed to an output device such as a computer or recorder.

2.3. The temperature programmer is capable of either holding the temperature of the sample environment constant (isothermal operation) or varying the temperature as a linear function of time, the rate of which is selectable (dynamic operation). In addition to isothermal or linear temperature ramp, a third option of modulated temperature programme has been applied to DSC and TGA.

2.4. The output device monitors directly the change of the property measured against both temperature and time in dynamic mode or temperature modulated mode or against time in isothermal mode.

3. **DEFINITION OF TERMS**

3.1. A number of terms are used to describe the various points of interest on the resultant plots when change of property is measured against temperature or time. The more commonly used terms are defined below and illustrated in figure A-1. For detailed definitions of characteristic temperatures see ASTM (American Society for Testing Materials) standards E1142 / E473.

3.2. T_g, the glass transition temperature, is measured at its mid-point. This is defined as the point at which the bisector of the angle made between the extrapolated baseline recorded before the transition and the extrapolated baseline recorded after the transition, intersects the DSC curve. At increasing temperature it is the temperature at which a polymeric explosive changes from a rigid glassy condition to a flexible rubbery state. Although most regular DSC/DTA users will recognize this, older material specifications for DTA/DSC techniques assumed that the T_g was based on the extrapolated onset, which is frequently 3-8°C colder than the current definition.

3.3. T_i, the initial temperature, is the temperature at which the first deflection from the base line is observed for a chemical reaction or a phase transition.

3.4. T_p, the peak maximum temperature, is the temperature at which the peak maximum or minimum is observed.

3.5. T_f, the final temperature, is the temperature, after a peak, at which no further deflection from the base line is observed.

3.6. T_m, the temperature of melting, is measured as the point of intersection of two tangents, one drawn to the curve before commencement of the event, the other to a point on the steepest part of the transition. The same principle may be applied to a solid-solid transition. This construction is only really relevant for pure crystalline materials – impure crystalline, or polymeric melts will take place over a temperature range and the leading edge of the peak will be curved. For the latter substances, T_m is determined as the intersection between the two tangent lines of the slopes of the endothermal peak.

3.7. T_e, the extrapolated onset temperature is measured as the point of intersection of two tangents, one drawn to the curve before commencement of the event, the other to a point on the steepest part of the transition. This parameter is mostly used in relation with exothermal effects.

3.8. ΔH_f, the heat of fusion, i.e. the amount of heat that is absorbed in the transition from the solid state to the liquid state, is under normal experimental circumstances (i.e. constant pressure)

equal to the enthalpy of fusion, indicated by ΔH_f (also called enthalpy of melting, indicated by ΔH_m). The heat effect associated with a solid-solid phase transition is under normal experimental circumstances equal to the enthalpy of transition, indicated by ΔH_{tr}. Both quantities are determined by measuring the area beneath the transitions.
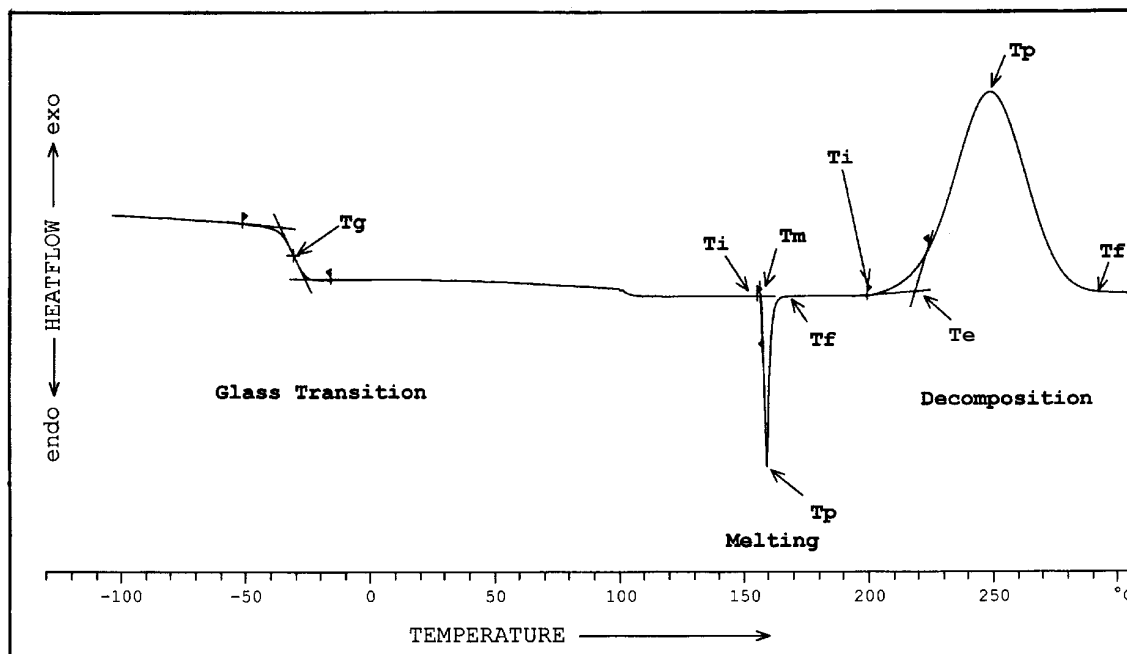

Figure A-1. Definition of terms of a DSC experiment

4. **PRINCIPLE OF OPERATION**

4.1. Differential Thermal Analysis, DTA

4.1.1. DTA records the difference in temperature (or in thermoelectric voltage) between a substance and a thermally inert reference material, when both are subjected to the same thermal conditions. Sample and reference holders are each fitted with their own temperature sensing device, usually thermocouples connected in opposition. Sample and reference holders are fitted to a heat sink (usually a metal block or wafer) which is surrounded by a single heat source (furnace) which can be programmed to raise the temperature of both sample and reference at a predetermined rate. A generalised DTA system is shown in figure E-1.

4.1.2. If there are no transitions or reactions occurring within the sample, the difference in temperature (ΔT) (or the corresponding thermoelectric voltage) between sample and reference is small and fairly constant. Temperature differences between the sample and reference are brought about by either endothermic or exothermic transitions or reactions within the sample pan. During endothermic transitions the sample undergoes "isothermal arrests", whereby its temperature remains relatively constant during the transition although there is an input of heat into the sample during this transition. The reference temperature continues to rise at the predetermined rate over this period hence a differential temperature exists between sample and reference, the sample lagging the reference. Conversely, during exothermic reactions, the heat evolved from the sample gives rise to a temperature difference between the sample and reference where the ΔT signal has the opposite polarity. These changes lead to a departure from the $\Delta T \approx 0$ baseline during transitions, resulting in a peak in the output signal. When the transition is over, the sample "catches up" with the reference and the signal returns to the baseline as was observed before the transition. A gradual return to the baseline is observed depending on thermal conductivity and heat capacity of the sample/crucible system. A jump or a change in slope of the baseline before and after the signal is caused by the difference in heat capacity and its temperature dependence between the original sample and the transition product.

4.2. Differential Scanning Calorimetry, DSC

4.2.1. This technique measures the difference between the heat flow to a sample and the heat flow to an inert reference while the temperature is controlled. Two general types of instrumentation can be used for measuring heat flow by differential scanning calorimetry - *Power Compensation DSC* and *Heat flow DSC*.

4.2.2. A **Power Compensation DSC** consists of individual sample and reference holders each fitted with its own heater and platinum resistance thermometer. In normal operation, the sample pan contains the explosive and the reference pan can be left empty or contain some inert material such as alumina. The system is operated by two electronic control loops. One is for the average temperature control, so that the temperature of sample and reference can be increased at a predetermined rate. The second loop ensures that if a temperature difference develops between reference and sample (due to exothermic or endothermic reaction in the sample) the power input is adjusted to remove this difference. Thus the temperature of sample and reference is kept close together by the continuous and automatic adjustment of the heater power of either the sample or the reference element depending on whether the sample undergoes exothermic or endothermic changes. Hence a signal is produced which is directly proportional to the difference between the heat input to the sample and that to the reference. The area beneath the curve is a direct measure of the heat involved in bringing about the transition i.e. heat flow to/from the sample (dH/dt) which is usually measured in milliwatts.

4.2.3. A schematic diagram of a power compensation DSC is shown in figure E-2(b).

4.2.4. **Heat flow DSC** (heat flux DSC) instruments operate on the DTA principle which can be represented as shown in figure E-1.

An important difference, however, is that in heat flow DSC instruments, there must be a well-defined thermal resistance between the wall of the furnace and the sample position of the sensor. In ideal circumstances exactly the same thermal resistance must be present between the wall of the furnace and the reference position of the sensor. This allows a more quantitative heat flow measurement to be achieved.

Mathematical transformation of the measured DTA signal is necessary to obtain values of heat flow to/from the sample to bring about the transition. The thermal analogue of Ohm's Law is used,

$$\frac{dH}{dt} = \frac{\Delta T}{R_{th}}$$

where dH/dt is the heat flow [W]

ΔT is the differential temperature [K]

R_{th} is the thermal resistance to heat flow between sample pan and holder [K·s·J^{-1}].

The heat flow to/from the sample is given by the difference in heat flows to the reference and sample holders.

$$\frac{dH}{dt} = \frac{dQ_s}{dt} - \frac{dQ_R}{dt}$$

where dQ_S = heat flow to sample

dQ_R = heat flow to reference

Applying the "thermal" Ohm's Law: $\dfrac{dH}{dt} = \dfrac{T_C - T_S}{R_{th}} - \dfrac{T_C - T_R}{R_{th}}$

where T_C is the temperature of the heat sink

T_S and T_R are the temperatures of the sample and reference respectively

$$\text{Thus, } \frac{dH}{dt} = \frac{T_R - T_S}{R_{th}}$$

The temperature difference given by the output from the two thermocouples connected in opposition is given by:

$$T_R - T_S = \Delta T \quad and \quad \Delta T = \frac{\Delta U}{S}$$

where ΔU is the thermocouple potential [µV]

S is the thermocouple sensitivity [µV K^{-1}]

It follows that,

$$\frac{dH}{dt} = \frac{\Delta U}{R_{th} * S}$$

dH/dt has a negative value for exothermic reactions and a positive value for endothermic reactions.

4.2.5. Recent instruments incorporate multiple thermal sensors increasing the number of terms in the equations above.

4.2.6. Both R_{th} and S are functions of temperature and can be combined as the calorimetric sensitivity. This is determined by calibration using the known heat of fusion of a standard reference material, such as biphenyl, indium, tin, or other pure metals, depending on the temperature of interest (see table G-1). The heat of fusion gives a measure of the measuring cell sensitivity in $\mu V\ mW^{-1}$. This term is also referred to as cell constant.

4.3.   Thermogravimetric Analysis (TGA)

4.3.1. TGA measures changes in weight of a sample as a function of temperature/time. Measurements can be carried out with a gas flow of air, nitrogen or another specified gas. The technique is useful in distinguishing phase changes from weight changes caused by chemical reactions. The technique becomes even more useful if connected directly to a FTIR or to a MS for evolved gas analysis (EGA). Gaseous decomposition products and volatile species can readily be identified making the task of characterising transitions in unknown compositions much simpler. Samples are weighed directly into a sample pan assembly fitted to the TGA or with an outer microbalance. The sample pan assembly is completely surrounded by a furnace for control of the sample temperature. It is possible to purge the furnace volume with inert or reactive atmospheres.

4.3.2. TGA is normally carried out using one of the schematic representations shown in figure E-3.

4.4   Heat Flow Calorimetry

4.4.1   HFC (also known as microcalorimetry) operates on the same principle as heat flow DSC (see chapter 4.2.4) with the difference that instead of one, a number of thermocouples are linked together at the sample and the reference holder thus increasing considerably the precision for measuring the temperature difference between both. This results in a much higher sensitivity of HFC compared to DSC. Instead of a furnace, a precisely temperature controlled system is used as heater. Sample sizes usually are in the gramme range instead of milligrammes as in DSC. Heat flow calorimeters are mostly operated at constant temperature. They are normally calibrated with an electric heater. In contrast to the dynamic methods where the explosives are usually completely decomposed during the experiment, HFC measurements are normally stopped at a low or moderate inversion level for safety reasons.

4.4.2   A schematic diagram of a heat flow calorimeter is shown in figure E-4.

4.5. General Summary

4.5.1. The processes detectable using the four principal thermal analysis techniques are summarised in table A-1.

Table A-1. Detectability of processes by different thermoanalytical techniques

Process	DTA	DSC	TGA	HFC
Phase transformation	+	+	-	-
Melting transitions	+	+	-	-
Purity	-	+	-	-
Sublimation / Evaporation	+	+	+	+ [1]
Glass transition	-	+	-	-
Heat capacity	-	+	-	+
Desorption	+	+	+	+ [1]
Adsorption	+	+	+	+ [1]
Chemical reaction	+	+	+	+
Decomposition	+	+	+	+
Oxidation/reduction	+	+	+	+

+ suitable method
- unsuitable method
1) in unsealed ampoules only; not used very often

NOTE 1: Processes such as sublimation may cause practical problems in that the sublimate will condense in the cooler parts of the instrument. Decontamination may be necessary at the end of each run performed and care must be exercised to prevent sublimates entering the internal workings of an instrument e.g. TGA balance or electronics. Efficient purging is, therefore, essential to minimise this possibility.

NOTE 2: Although thermal analysis techniques can be used to determine glass transition, they may not necessarily be the best technique available. During a glass transition the mechanical properties of the sample change very drastically and therefore mechanical analysis techniques, for example Dynamic Mechanical Analysis (DMA) or Thermomechanical Analysis (TMA), may prove to be more suitable. DMA is more sensitive by orders of magnitude for T_g measurement than DSC and should be recommended if sample size permits.

NOTE 3: Some heat flow calorimeters can be equipped with special titration or controlled humidity channels where heats of dissolution, desorption, adsorption, etc. can be monitored very sensitively and specifically.

5. **GENERAL CONSIDERATIONS IN PERFORMING THERMOANALYTICAL STUDIES OF EXPLOSIVE MATERIALS**

5.1. Safety of the operator is of primary importance and analyses will generally be carried out on the smallest sample size necessary.

5.2. Heating rates or isothermal test temperatures shall be carefully chosen to ensure that the decomposition reactions are controlled and do not lead to thermal runaway or ignition of samples. The only exception to this is for the study of ignition reactions of primary explosives, black powders or pyrotechnics using DTA, when heating rates of up to 50°C/min have to be used. Serious damage to TGA and DSC instruments is likely to occur if reactions are not carried out under controlled conditions. In a heat flow calorimeter with too large samples the damage may be severe.

5.3. In hermetically closed sample containers many explosives decompose much more violently than in open crucibles due to increasing pressure.

5.4. Generally, most analyses not using hermetically closed sample containers shall be performed in a stable flow of an inert gas. This is necessary for a number of reasons:

   (i) To purge away evolved gases, protecting the cell from corrosive products.

   (ii) Displacement of atmospheric oxygen to avoid unwanted oxidation.

   (iii) To purge away evolved gases which may upset the equilibrium of certain chemical reactions.

   (iv) As a carrier to FTIR in TGA/evolved gas analysis (EGA) or mass spectrometry (MS).

5.5. Some materials e.g. pyrotechnics, rely on the presence of air for their preferred reaction to proceed. Careful consideration of sample reactions will have to be conducted before deciding on the gas environment to be used.

5.6. The physical characteristics of samples can also influence observations made. Pressed samples behave differently to loose powders. The degree of compaction of the sample can also affect the course of the reaction. Particle size will also affect the results as the rate of reaction may be highly dependant on the surface area. Hence sample preparation is of paramount importance and must be prescribed if the results are to be used for comparison purposes. Generally primary explosives are used without further treatment. The individual components of pyrotechnics may separate during storage. Careful mixing is advisable prior to removal of the sample for analysis. Generally the sample can then be used without further treatment.

5.7. Processes involving the weighing of samples and the handling of sample crucibles should be conducted using non-sparking tools and implements (e.g. spatulas). These should be made of either phosphor-bronze, ceramic or electrically conductive polymer material.

5.8. It is preferable that dynamic measurements are started at room temperature. However there may be occasions when it is necessary to start the measurement at lower temperatures; for example when measuring the glass transition of nitrocellulose. Never place explosive materials into a hot furnace. Never attempt to remove samples from the thermal equipment until ambient temperature has been restored. Cooling accessories may be used to facilitate cooling of the sample environment/furnace.

5.9. Recommended heating rates and sample sizes for the different types of explosive materials are given in tables A-2 to A-4:

Table A-2. Test conditions for the dynamic measurement of explosives (except primary explosives)

EXPLOSIVE MATERIAL	TEST TECHNIQUE			RECOMMENDATIONS
	DTA	DSC	TGA	
Secondary detonating explosives	+	+	+	5 mg maximum weight.
PBX	+	+	+	10°C min^{-1} maximum heating rate.
Propellants	+	+	+	
Pyrotechnics	+	+	+	sample size maximum 10 mg and heating rate 10°C min^{-1} maximum.
Black Powder	+	+	+	or sample size maximum 20 mg and heating rate 5°C min^{-1} maximum

Table A-3. Test conditions for the dynamic measurement of primary explosives

PRIMARY EXPLOSIVE	TEST TECHNIQUE	TEST CONDITIONS	RECOMMENDATIONS
Unknown mixture	DSC DTA TGA	Sample size 1 mg maximum Heating rate max. 10°C min^{-1}	DTA is the most robust of these techniques.
Less well characterised primary explosives	DSC DTA TGA	Sample size 2 mg maximum Heating rate max. 5°C min^{-1}	When using the DSC technique, to prevent over pressurisation of the pans they should not be sealed or the lid should be pierced.
Well characterised primary explosives	DSC DTA TGA	Sample size 2 mg maximum Heating rate max. 5°C min^{-1}	These conditions should only be used by experienced operators.

Table A-4. Test conditions for the isothermal measurement of explosives in a heat flow calorimeter.

EXPLOSIVE MATERIAL	TEST TEMP.	SAMPLE SIZE	RECOMMENDATIONS
Unknown explosives	See NOTE 6	Max. 200 mg	Check by DSC and oven test first. (see Annex B, procedure 4)
Primary explosives	See NOTE 6	Max. 200 mg	Preliminary DSC or DTA test recommended
High explosives	See NOTE 6	See NOTE 5	Check by DSC and oven test first. (see Annex B, procedure 4)
PBX Propellants	See NOTE 6	See NOTE 5	Carefully study influence of oxygen and moisture and closing on the results
Pyrotechnics Black Powder	See NOTE 6	See NOTE 5	Carefully study influence of oxygen and moisture on the results

NOTE 4: The maximum sample size and heating rates quoted in tables A-2 and A-3 are based on experimentation, but with due consideration to both safety to the operator and damage to the equipment. It has been found that the sample sizes quoted were able to provide measurable, homogeneous and representative samples that were small enough to ensure safety to the operator and to the equipment.

NOTE 5: The maximum sample size in a heat flow calorimeter depends on the design of the calorimeter, the explosives type and the measuring temperature. Large samples or higher temperatures may be used for well-known explosives but it should be taken into account that both variations increase the tendency for runaway reactions.

NOTE 6: As a rule of thumb the maximum temperature of the HFC measurement should be at least 60°C below the extrapolated onset temperature (T_e) of the lowest exotherm as estimated by DSC in a hermetically closed crucible at maximum heating rate H of 2°C·min^{-1}.

Measuring at or below this estimated temperature will reduce the risk of suddenly occurring runaway reactions, but frequent observation of the signals is strongly recommended.

5.10   By carrying out thermal investigations within the recommended limits, the possibility of explosion, thermal runaway and risk of damage to equipment will be minimized but never totally excluded. As a general rule the possibility of explosion will diminish with smaller sample sizes, lower heating rates and lower temperatures.

5.11   It is also essential to use a fume extraction system in close proximity to the instruments to remove any harmful evolved gases resulting from decomposition reactions.

TEST PROCEDURES

1.   **PROCEDURE 1. DIFFERENTIAL THERMAL ANALYSIS**

1.1.   Apparatus for all DTA applications

1.1.1.   A Differential Thermal Analyzer automatically recording the differential temperature or the differential thermoelectric voltage between sample and reference materials with the required sensitivity and precision.

1.1.2.   Sample crucibles should be manufactured from material which is inert to the material under test. They should be robust enough to withstand the mechanical forces and high temperatures encountered during ignition reactions. In special investigations (e.g. autocatalysis), a loosely fitting lid or a pierced lid can be used. Ceramic materials or platinum are considered suitable. Ceramic is the preferred material since the crucibles are readily cleaned in a muffle furnace or by boiling in concentrated acids.

1.1.3.   Purge gas supply and associated flow controller if required.

1.1.4.   Inert reference material which is not thermally active over the temperature range to be used. For most applications, alumina has been found to be suitable.

1.1.5.   Balance capable of measuring to at least 0.1 mg.

1.2.   Calibration

1.2.1.   If a DTA instrument is used only semi-quantitatively for measurement of endothermic and exothermic transitions, accurate calibration of the heat of transition reaction is not generally necessary.

1.2.2.   Calibration should be performed to the level recommended by the instrument manufacturer but shall not exceed ± 1°C for a post-calibration check until 600°C. Generally, temperature calibration will be performed at at least two points using standard reference materials with melting point onset close to the limits of the temperature range of interest (see table G-1). The use of solid-solid phase transitions for calibration is less reliable.

1.2.3.   Calibration will be carried out using the same type of sample crucible, heating rate, purge gas and purge gas flow rates as will be used for test measurements.

1.2.4.   Typical standard reference materials used for temperature and enthalpy calibration are shown in Annex G.

1.3.   Sample preparation

Samples shall be representative of the material being studied and should be prepared to achieve good thermal contact between the sample and container. Multiple runs may be necessary to demonstrate reproducibility of the sample.

1.4.   Procedure

1.4.1.   Weigh the recommended quantity of a representative portion of the sample to at least 0.1 mg into a tared crucible and record the sample weight.

1.4.2.   Load the sample and reference crucibles into the instrument.

1.4.3.   Purge the sample chamber with an appropriate gas and record the flow rate.

NOTE 7.   Temperatures of ignition are generally performed in static air with no purge gas.

1.4.4.   Heat the sample at the recommended heating rate over the temperature range of interest and record the thermal curve produced.

1.4.5.   Repeat using a further representative portion of the sample after allowing the furnace to cool to room temperature.

1.5.   Analysis

Figure F-1 of annex F shows a typical DTA thermal curve and indicates some typical data points that can be determined.

1.6   Reporting

Examine the thermal curve and report extrapolated onset temperature and peak maxima of any endothermic or exothermic events. Wherever possible identify the thermal effect.

Use the Data Sheet as shown in Annex D.

2. **PROCEDURE 2. DIFFERENTIAL SCANNING CALORIMETRY**

2.1   Apparatus

2.1.1   Differential Scanning Calorimeter automatically recording the differential heat flow or the differential electric heating power between the sample and reference materials with the required sensitivity and precision. It should have an upper temperature capability of at least 500°C.

2.1.2   Sample crucibles should be manufactured from materials which are inert to the material under test and of high thermal conductivity. Typical materials include aluminium, gold, platinum and ceramics. Aluminium is the most commonly used material because of its lower cost.

2.1.3   Purge gas supply and associated flow controller.

2.1.4   Generally, it is not necessary to use a reference material in the reference crucible. However where a reference is considered necessary, an inert reference material which is not thermally active over the temperature range should be used. For most applications, alumina has been found to be suitable.

2.1.5   Balance capable of measuring to at least 0.01 mg.

2.1.6   Crucible sealing press.

2.2   Calibration

2.2.1.   Calibration is performed by measurements of the heats of fusion and melting points of standard reference materials. The instrument is calibrated using the same type of sample crucible, heating rate, purge gas and purge gas flow rates as will be used for the test measurements.

2.2.2.   Typical standard reference materials used for temperature and enthalpy calibrations are shown in Annex G.

2.2.3.   Calibration should be performed to the level recommended by the instrument manufacturer. Post-calibration deviation in melting point or solid-solid phase transition onset shall not exceed ± 0.5°C and heats of fusion of ± 2%.

2.3.   Sample preparation

2.3.1.   Samples shall be representative of the material being studied and should be prepared to achieve good thermal contact between the sample and container. Multiple runs may be necessary to demonstrate reproducibility of the sample.

2.4.   Procedure

2.4.1.   Weigh accurately the recommended quantity of a representative portion of the sample into a container tared together with lid.

2.4.2.   If necessary for the application, seal the lid onto the crucible using the sealing press. Reweigh the container plus any cut residue and record the sample weight.

> NOTE 8.   For some applications (e.g. substances sensitive to oxidation), it may be necessary to hermetically seal the crucible under an inert gas atmosphere.

> For most applications standard crucibles and lids will be used. These generally cannot withstand internal pressures of > 2 atmospheres and effectively allow the release of evolved gases without the risk of explosion.

Alternatively the lid can be pierced with a pin. This can prevent distortion and resultant poor contact with the sensor.

2.4.3. Load the sample and reference material crucibles into the instrument.

2.4.4. Purge the sample chamber with the inert gas at the flow rate recommended by the manufacturer and record the gas flow rate.

2.4.5. Heat the sample at a rate complying with tables A-2 and A-3 over the temperature range of interest and record the thermal curve produced.

> NOTE 9. The upper temperature limit is governed by the instrument being used and also the crucible material. Some instruments have an upper temperature limit of 600°C but most can be used to 725°C. However, with these instruments, an upper temperature limit of 600°C is recommended if using Al crucibles as aluminium melts at 660.2°C. It is not generally advisable to take DSC equipment above 500°C unless the analysis requires it. Higher temperatures shorten the cell's lifetime.

2.4.6. Repeat, using a further representative portion of the sample, when the furnace has returned to room temperature.

2.5. Analysis

2.5.1. Figure F-2 of annex F shows a typical DSC thermal curve and indicates some typical data points that can be determined.

2.6. Reporting

2.6.1. Examine the thermal curve and report onset temperatures and peak maxima of any endothermic or exothermic events. Wherever possible, identify the thermal effect.

2.6.2. When reporting and interpreting data, consideration should be given to the following points (use the Data Sheet in Annex D):

2.6.2.1. Under the test conditions quoted it is doubtful whether the heat of fusion of some explosive materials can be measured using DSC. For example, RDX decomposes upon melting and, therefore, endothermic fusion and exothermic decomposition occur simultaneously and the magnitudes of both peaks are obviously affected.

> NOTE 10. Some test centres have noted that heat of fusion for RDX can be separated from decomposition by using a higher heating rate or modulated temperature techniques.

2.6.2.2. Care should also be exercised with the initial melting peak observed at about 78°C in RDX/TNT mixtures. This peak is due to the melting of the RDX/TNT eutectic consisting of 2% RDX/98% TNT and not the melting transition of TNT. The remaining 2% TNT melts at about 80°C and is not observed since it is contained within the melting range of the eutectic. For most RDX/TNT compositions, all of the TNT present melts as part of the eutectic.

3.   **PROCEDURE 3. THERMOGRAVIMETRIC ANALYSIS**

3.1.   Apparatus

3.1.1.   Thermogravimetric analyzer automatically recording weight loss/gain as a function of temperature. It should be capable of weighing to 0.01 mg.

3.1.2.   Sample crucibles should be manufactured from material which is inert to the material under test. Typical materials include ceramic, platinum and aluminium. Ceramic is the preferred material since the crucibles are readily cleaned in a muffle furnace or by boiling in concentrated acids. The use of aluminium pans limits the upper temperature to 600°C, but is adequate for many applications.

3.1.3.   Purge gas supply and associated flow rate controller.

3.2.   Calibration

3.2.1.   The balance should be calibrated according to the manufacturer's instructions.

3.2.2.   Temperature calibration is achieved by measurement of the melting points of standard reference materials in the form of fusible links, by measurement of the Curie point temperatures of standard materials (i.e. loss of ferromagnetic properties) or by any other suitable method. Curie elements change their ferromagnetic properties at a certain temperature. This is converted into a TGA signal using an external permanent magnet.

> NOTE 11.   Fusible links are short lengths of pure metal wire connected to the balance pan and carrying a small weight. When the metal melts, a weight change is experienced by the balance.

3.2.3.   Typical standard reference materials used for melting point temperature calibrations are shown in table G-1.

3.2.4.   Typical standard reference materials used for Curie point temperature calibration are shown in table B-1:

Table B-1. Typical standard reference materials used for Curie point temperature calibration

Material	Curie point (°C)
Nickel	357.0
Trafoperm[1]	745.6

[1] Trafoperm is available from Mettler Toledo as a ready prepared calibration material.

3.2.5.   Calibration should be performed to the level recommended by the instrument manufacturer but shall not exceed a deviation in transition temperatures of ± 5°C.

3.3.   Sample preparation

Samples shall be representative of the material being studied. Multiple runs may be necessary to demonstrate reproducibility of the sample.

3.4.   Procedure

3.4.1.   Purge the sample chamber with inert gas and record the gas flow rate.

3.4.2.   Tare the balance.

3.4.3. Introduce the sample into the sample crucible.

3.4.4. Record the sample weight.

3.4.5. Heat the sample at the recommended heating rate over the temperature range of interest. Record any weight changes experienced by the sample as a function of temperature.

3.4.6. Allow the furnace to cool and repeat the complete procedure again, using a further representative portion of sample.

3.5. Analysis

Figure F-3 of annex F shows a typical TGA thermal curve and indicates some typical data points that can be determined.

3.6. Reporting

3.6.1. Weight losses/gains between the start and end of reaction should be calculated as a percentage. Weight loss steps between plateau regions should be measured as percentages and, wherever possible, weight loss steps should be assigned to thermal effects e.g. loss of volatile matter, decomposition, etc. Use the Data Sheet as outlined in Annex D.

3.6.2. The derivative weight loss trace should also be recorded and presented. This is a measure of the rate of weight loss as a function of time/temperature and is characteristic for a material or composition. It generally consists of a series of peaks, each corresponding to a weight loss/gain step. It can be used as a thermogravimetric "fingerprint" for characterisation purposes. Record the peak temperatures of the derivative TGA trace.

4.   **PROCEDURE 4. HEAT FLOW CALORIMETRY (HFC)**

WARNING: Since in HFC considerably larger sample weights are commonly used, extreme care must be applied for selection of test conditions to avoid the risk of explosions. At least, if samples of unknown or less well characterized explosives have to be measured preliminary testing is necessary. The following procedure to find a still safe temperature for a given sample size is recommended:

- Run a small scale dynamic DSC test in a closed container at a heating rate of 2°C/min.

- Subtract at least 60°C from the extrapolated onset temperature of the first exotherm.

- Store the sample in a container as it should be used in the HFC at this temperature and for at least the same time as planned for the HFC measurement in a rugged oven.

4.1   Apparatus

4.1.1   Heat flow calorimeter automatically recording the differential heat flow between the sample and reference materials.

4.1.2   In most cases sample vessels that can be hermetically sealed are used. It must be proved that the vessel material does not react with the sample and its decomposition products. In case of measuring adsorption or desorption processes an open or semi-closed sample vessel is used.

4.1.3   Appropriate data collecting and calculating system including integration.

4.1.4   If possible, operate the calorimeter remotely.

4.2   Calibration

4.2.1   The calorimeter is usually calibrated using an electric heater.

4.2.2   Up to now, chemical or physical standards for the calibration of calorimeters are not common.

4.3   Sample preparation

4.3.1   As far as possible the sample should be measured in its original condition.

4.3.2   The sample should be representative of the batch or lot in test. If the volume of the sample vessel is too small to fulfill this, a sufficiently large amount of the sample should be ground or cut and the sample should be taken from a well mixed fraction as near as possible between 1 - 2 mm.

4.3.3   As the influence of atmospheric oxygen, pressure and the evolved gases (mainly NO_x) are not negligible, it is recommended to run the tests under conditions as close as possible to those in munitions. Therefore the decision, whether the ampoule should be completely filled and hermetically sealed or not, must be made carefully.

4.4   Procedure

4.4.1   Set the calorimeter to the desired temperature, wait until baseline is stable and calibrate.

4.4.2   Decide under which conditions (closed / not closed; filled / not filled …) the measurements shall take place and which ampoule type shall be taken.

4.4.3   Weigh in the sample and place the ampoule into the calorimeter. Start the measurement immediately.

4.4.4   Stop the measurement, if gas leaking (see e.g. Fig. B-1 in STANAG 4582) or if the beginning of severe autocatalysis is indicated.

4.4.5   After the end of measurement remove the sample from the calorimeter and let it cool to ambient temperature. Reweigh sample to detect mass losses due to gas leaking.

4.5   <u>Analysis</u>

4.5.1   Figure F-4 in Annex F shows a typical HFC curve.

4.5.2   The data must be normalised to one gram of explosive.

4.5.3   A combination of heat flow calorimetry with chemical analyses of the sample (and possibly of the reaction gases) after measurement is helpful for the understanding of degradation processes. One example is the analysis of stabilizer content in nitrocellulose based propellants.

4.5.4   Procedures for kinetic evaluation are described in Annex C.

4.6   <u>Reporting</u>

Report the results in the form outlined in Data Sheet in Annex D. Provide separate copies of the heat flow diagram for each sample.

FURTHER INVESTIGATIONS POSSIBLE USING THE TECHNIQUES DESCRIBED

1. ISOCONVERSIONAL KINETIC ANALYSIS

GENERAL

The aim of thermal analysis is frequently to assess the stability of explosives at temperatures far below the experimental range. This requires measurements at at least 3 different temperatures or heating rates followed by kinetic analysis.

1.1 Formal kinetics

Kinetic analysis of reactions based on mass loss or heat flow measurements allows formulation of the conversion or its rate as function of temperature and time ("formal kinetics"). If not combined with techniques for chemical analysis, the procedures do not identify reaction products.

However, the main goal of kinetics, when applied to explosives, is to assess their functioning and safety life time. Both can be sufficiently well predicted by formal kinetics.

Even though in fact most decompositions are more complicated, the following general equation is at least approximately valid in many cases (especially if low conversion levels have to be considered, as for functional life predictions).

General equation:

$$d\alpha/dt = f(\alpha) \cdot A \cdot e^{-E/RT} \qquad \text{(eq. C-1)}$$

α	=	Conversion (reduced to a scale from 0 to 1)
t	=	Reaction time [s]
A	=	Frequency factor [s^{-1}]
E	=	Activation energy [kJ/mole]
T	=	Reaction temperature [K]
R	=	Gas constant (= 0.00831447 kJ/(mole $\cdot$ K))
$f(\alpha)$	=	Reaction model

1.2 Estimation of activation energy

When large calibre munitions are stored at elevated temperatures an exothermal decomposition of the explosive may cause an internal temperature increase and consequently an accelerated ageing, which in worst case may end in a thermal explosion. For simulation of such a scenario, complete formal kinetics (including type and parameters of the reaction model, obtained from measurements up to extensive conversion) and support by additional quantities such as heat conductivity are required.

For prediction of ageing at moderate temperatures, where the exothermal decomposition reaction is slow and the internal temperature increase is small, it is sufficient to estimate only the activation energy.

For this purpose several isoconversional procedures have been developed all based on the same principle:

At a fixed conversion level (= the same mass loss or same area below a heat flow curve), the reaction models and all functions derived from them have constant values. They are incorporated in a pseudo

frequency factor (A') which is only constant for this conversion. The slope from a plot of the natural logarithm of different variables against the reciprocal absolute temperature gives the activation energy. Its constancy can be controlled by a series of plots at different conversion degrees. Some frequently used procedures are listed in Table C-1.

Table C-1. Examples of procedures for isoconversional estimation of activation energy

$$\ln y = A' + B/T \qquad \text{(eq. C-2)}$$

Author	Reference	y	B	Applicable for DSC, HFC and TGA in
Friedman	[1]	$d\alpha / dt$	$- E/R$	dynamic and isothermal mode
Kissinger	[2]	heating rate/T^2	$- E/R$	dynamic mode
CNG U. Ticmanis a.o.		time	$+ E/R$	isothermal mode

To get reliable results, some rules for optimizing the experimental conditions can be given:

(a) Try to achieve about a 10-fold variation of the maximum conversion rate.

In the dynamic operation mode this is easily realized by using the same variation of the heating rate. So if only 3 measurements are performed a sequence of 0.1/0.3/1°C·min^{-1} would be adequate, as well a sequence of 0.1/0.2/0.5/1°C·min^{-1} for series of 4 measurements. (Don't use constant differences in heating rate e.g. 0.1/0.4/0.7/1°C·min^{-1}).

Optimal variation of test conditions when performing isothermal experiments depends on the temperature range where the reaction is measured and on its activation energy. The following operation sequence may help:

Perform measurements at 2 suitable temperatures differing by 10°C, estimate a provisional value for E and calculate the required total temperature variation ΔT from

$$\Delta T = \frac{1}{\dfrac{1}{T} - \dfrac{R * ln10}{E}} - T \qquad \text{(eq. C-3)}$$

where T is the mean temperature of both measurements [K]

Perform the additional experiments according to ΔT and using approximately constant temperature differences between the measurements.

(b) Avoid too high heating rates which cause an increase of the internal sample temperature against that measured outside of the sample container and consequently a falsification of the calculated activation energy. This is a generally underestimated point of view in dynamic thermal analysis when used for kinetic evaluation. Overheating of the sample is indicated by increased values of E calculated by Friedman analysis from the two highest heating rates.

1.3 Predictions

For a given experimental conversion degree in an isothermal measuring the corresponding experimental time (t_{exp}) and temperature (T_{exp}) can be extrapolated to ambient conditions leading to the same conversion by

$$t_{amb} = t_{exp} * e^{\frac{E}{R}(\frac{1}{T_{amb}} - \frac{1}{T_{exp}})} \qquad \text{(eq. C-4)}$$

and

$$T_{amb} = \frac{1}{\frac{R * ln(t_{amb}/t_{exp})}{E} + \frac{1}{T_{exp}}} \qquad \text{(eq. C-5)}$$

(t_{amb} results in the same unit as t_{exp}, T_{amb} in K)

For conversions from dynamic measurements use

$$t_{amb} = \frac{1}{H} * e^{\frac{E}{RT_{amb}}} * \int_{T_{0,exp}}^{T_{exp}} e^{\frac{-E}{RT}} dT \qquad \text{(eq. C-6)}$$

where:

H = heating rate [°C·min^{-1}]

$T_{0,exp}$ = starting temperature of dynamic experiment [K]

(t_{amb} results in min, T_{amb} in K)

and

$$T_{amb} = \frac{E}{R * ln\left[\frac{t_{amb} * H}{\int_{T_{0,exp}}^{T_{exp}} e^{\frac{-E}{RT}} dT}\right]} \qquad \text{(eq. C-7)}$$

For extrapolations choose conversion points from curves which are about in the middle of the experimental temperature or heating rates range.

1.4 Uncertainty of prediction

The errors in predictions from experimental to ambient conditions mainly increase with the error of the calculated value of the activation energy and the difference between ambient and experimental temperature.
If the experiments are performed following the guidelines given above the error should be not more than ±10 kJ/mole, independent of the absolute value.

With this conservative assumption the errors in prediction can be calculated from eq. C-4 to C-7. If we assume additionally a heating rate of 0.5°C/min for evaluation of dynamic experiment and an evaluation time t_{exp} of 10 days for an isothermal HFC measurement the following uncertainty of predictions results for an explosive of sufficient stability for which a just tolerable decomposition is calculated for 20 years at 25°C (t_{amb}= 20 years, T_{amb}= 25°C):

Table C-2. Uncertainty of predictions for ambient conditions

E [kJ/mole]	T_{exp} [°C]	Mode	Eq.	t_{amb}, calculated [y]	t_{amb}, error range [y]	Eq.	T_{amb}, calculated [°C]	T_{amb}, error range [°C]
100	83.3	iso	C-4	20	14-28	C-5	25.0	22.6-27.5
100	163.3	dyn	C-6	20	11-36	C-7	25.0	20.6-29.4
200	51.5	iso	C-4	20	17-24	C-5	25.0	24.4-25.6
200	86.6	dyn	C-6	20	15-28	C-7	25.0	23.8-26.2

With increasing stability (higher T_{exp} to achieve the decomposition) the error range of both time and temperature predictions also increases considerably. But this should normally be of low practical relevance because the true stability will still be more than sufficient.

References

[1] H.L. Friedman, "Kinetics of thermal degradation of char-forming plastics", *J. Polym. Sci.* C6, 183 (**1963**).

[2] H.E. Kissinger, *Anal. Chem.* 29, 1702-1706 (**1957**).

2   FURTHER APPLICATIONS

2.1   Purity programs applied to DSC melting transitions of components can give useful information on the identity and purity of major components provided impurities are dissolved in the liquid phase of the component under study.

2.2   Heats of fusion can be used to estimate the quantitative composition of known mixtures. Only DSC can be used to study heats of fusion.

2.3.   Under suitable conditions DSC can provide a quick and convenient procedure for the determination of specific heat capacity.

2.4   All techniques described in this STANAG are suitable to determine the compatibility of explosives with contact materials. Details are described in STANAG 4147.

NATO STANAG 4515 DATA SHEET 1 (Side A)
(for DSC, DTA and TGA)

Report Reference Number:

(Unique Reference Number)   Page __ of __ Page(s)

TEST SITE INFORMATION	TEST CONDITIONS
Laboratory:	Instrument Model:
Date:	Temperature Range:
Test Procedure:	Heating Rate:
Date Tested:	Type of sample container
POC:	(Material, closed-pierced-open)
	Purge Gas:
	Purge Gas Flow Rate:

SPECIMEN INFORMATION	SAMPLE PREPARATION
Sample designation:	Sample preconditioning and preparation details:
Sample source/Manufacturer:	
Lot or ID No:	COMPOSITION
Date of Manufacture or Receipt:	Component and percentage details:
Form of material:	
Sample weight:	
Particle size:	DATA SENT TO

NATO STANAG 4515 DATA SHEET 1 (Side B)

(for DSC, DTA and TGA)

Report Reference Number:

(Unique Reference Number)   Page __ of __ Page(s)

RESULT SUMMARY

TEMPERATURE (°C)	OBSERVATIONS
	Key T_g = Glass Transition Temp. T_p = Peak Max Temperature
	T_i = Initial Temperature T_e = Extrapolated Onset Temp. (decomp.)
	T_m = Melting Temperature T_f = Final Temp.
	ΔH_f = Heat of Fusion

THERMAL CURVE

Insert or attach

COMMENTS

NATO STANAG 4515 DATA SHEET 1 (Side A)

Report Reference Number: **EXAMPLE**

Page 1 of 2 Pages

TEST SITE INFORMATION	TEST CONDITIONS
Laboratory: DRA Chorley	Instrument Model: TA Instruments 910 DSC
Date of Report: 19th March 96	Temperature Range: 50 - 300°C
Test Procedure: DSC	Heating Rate: 10°C min^{-1}
Date / Period of Test: 18th Sept 95	Type of sample container: pierced aluminium pan
POC:	Purge Gas: Nitrogen
	Purge Gas Flow Rate: 80 cm^3 min^{-1}

SPECIMEN INFORMATION	SAMPLE PREPARATION
Sample designation: EDC1	Sample preconditioning and preparation details:
Sample source/Manufacturer:	None

	COMPOSITION
Lot or ID No:	Component and percentage details:
	HMX 70%
Date of Manufacture or Receipt:	TNT 25%
	RDX 4%
Form of material:	Beeswax 1%
Sample weight: 1.7820 mg	

	DATA SENT TO
Particle size	

NATO STANAG 4515 DATA SHEET 1 (Side B)

Report Reference Number: **EXAMPLE**

Page 2 of 2 Pages

RESULT SUMMARY

TEMPERATURE (°C)	OBSERVATIONS
	Phase Transition Reaction
	Key T_g = Glass Transition Temp. T_p = Peak Max Temp.
	T_i = Initial Temp. T_e = Extrapolated Onset Temp. (decomp.)
	T_m = Melting Temp. T_f = Final Temp.
	ΔH_f = Heat of Fusion
77.3	Onset of melting RDX/TNT eutectic. (T_m)
80.1	RDX/TNT eutectic melting transition peak max. (T_p)
195.6	Onset of melting of RDX. (T_m)
210.7	Decomposition exotherm onset. (T_i)
277.1	Decomposition exotherm max. (T_p)
295.5	Decomposition exotherm end. (T_f)

THERMOGRAM

DSC

Sample : EDC 1 REFERENCE SAMPLE
Size : 1.7820 MG
Method : PDX
Comment : N2 PURGE GAS 80 MLS/MIN

File : KMDSC.010
Operator : KMD
Run Date : 18-SEP-95 16:25

COMMENTS

NATO STANAG 4515 DATA SHEET 1 (Side A)

(for HFC)

Report Reference Number:

(Unique Reference Number)   Page __ of __ Page(s)

TEST SITE INFORMATION	TEST CONDITIONS
Laboratory:	Calorimeter Model:
Date:	Material of vessel:
Test Procedure:	Volume of vessel [cm³]:
Date Tested:	Sample weight [g]:
POC:	Calibration range [µW]:
	Test temperature [°C]:
	Total measurement duration [d]:

SPECIMEN INFORMATION	SAMPLE PREPARATION
Sample designation:	Sample preconditioning and preparation details:
Sample source/Manufacturer:	
Lot or ID No:	**COMPOSITION**
Date of Manufacture or Receipt:	Component and percentage details:
Form of material:	
Sample weight:	
Particle size:	**DATA SENT TO**

NATO STANAG 4582 DATA SHEET 2 (HEAT FLOW CALORIMETRY) SIDE B			
Report Reference Number: (Unique Reference Number)			Page 2 of 2 Page(s)
RESULTS			
Sample No	1	2	3
Heat release until time of evaluation [J/g]			
Max. heat flow (P_m) [1] within time of evaluation [µW/g]			
Time of evaluation calculated by eq. 2 [d] [1]			
Heat flow limit calculated by eq. 3 [µW/g] [1]			
HFC CURVE			
COMMENTS			

[1] for nitrocellulose based propellants only. Please refer to STANAG 4582 for equations and limit values.

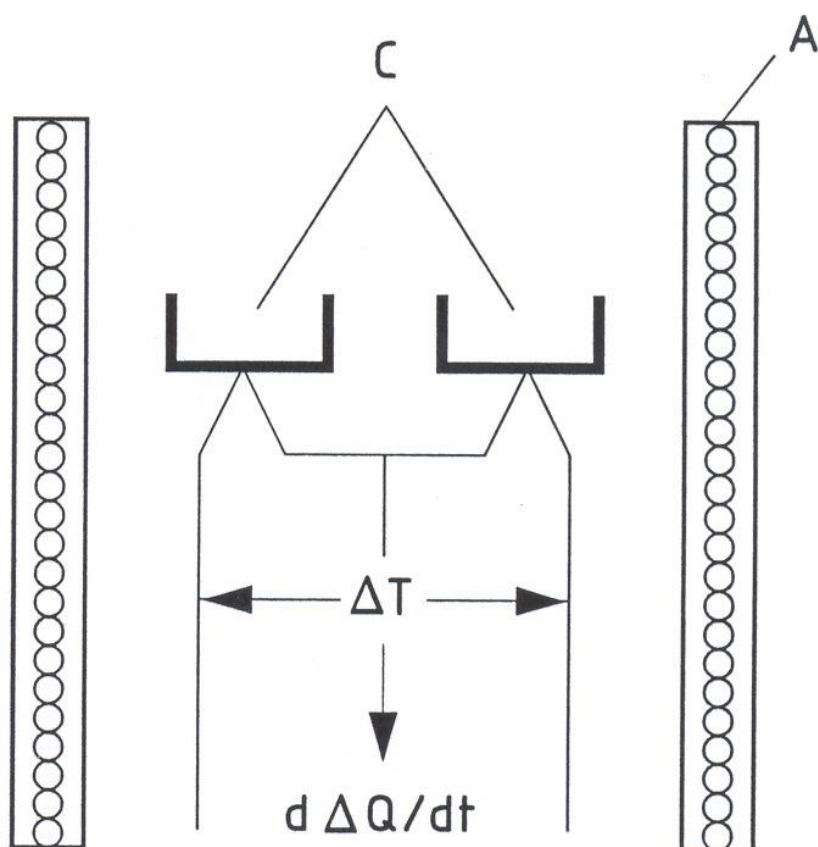**SCHEMATIC DIAGRAMS OF APPARATUS USED FOR THERMAL ANALYSIS**

Figure E-1. Schematic diagram of a DTA apparatus

(a)
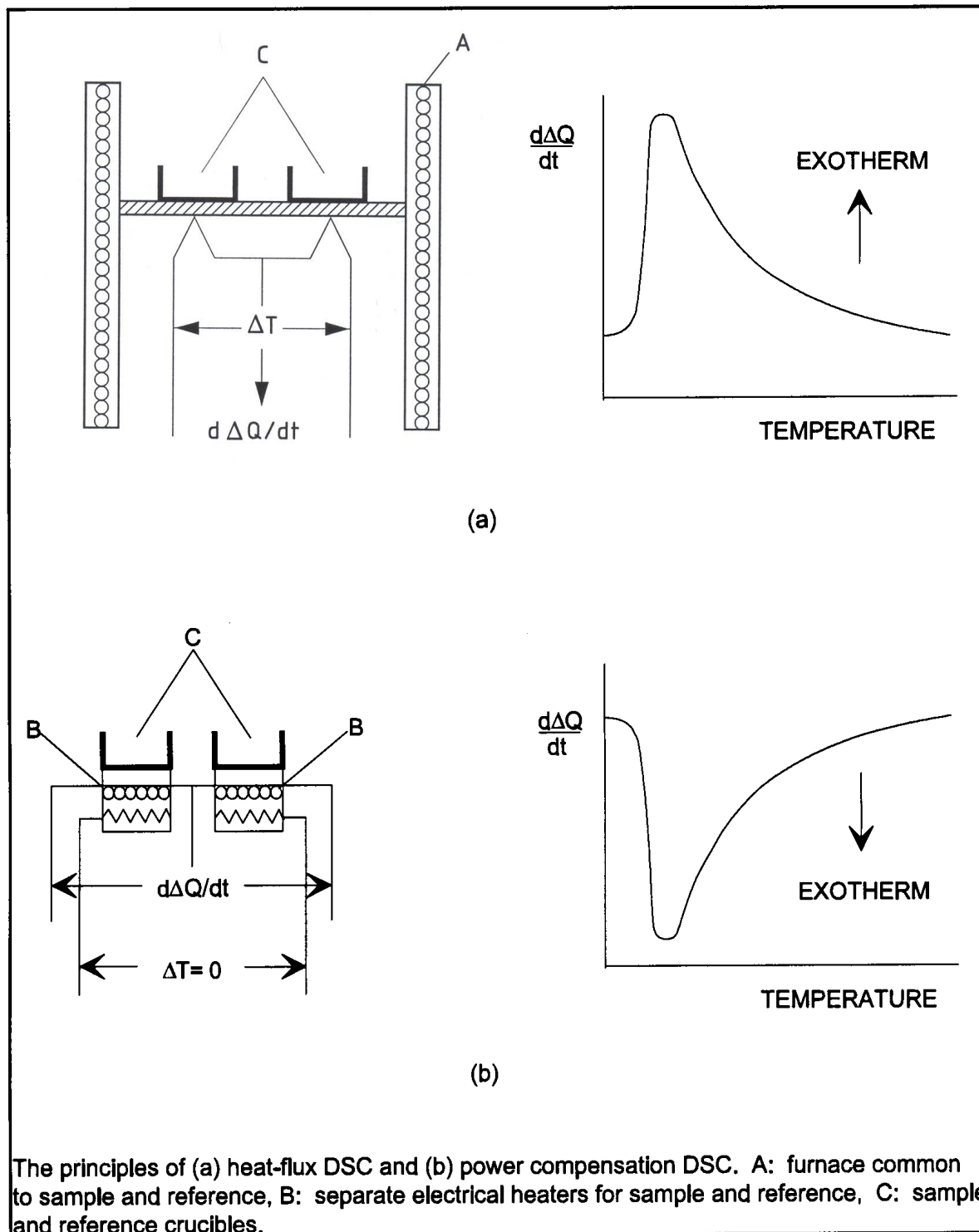
(b)

The principles of (a) heat-flux DSC and (b) power compensation DSC. A: furnace common to sample and reference, B: separate electrical heaters for sample and reference, C: sample and reference crucibles.

Figure E-2. DSC operating principles

Horizontal
thermobalance

Top - loading vertical
thermobalance
(fixed support)

Top - loading vertical
thermobalance
(counterbalanced support)

Bottom - loading vertical
thermobalance

Microfurnace   External
                furnace

Symmetrical
bottom - loading
vertical thermobalance

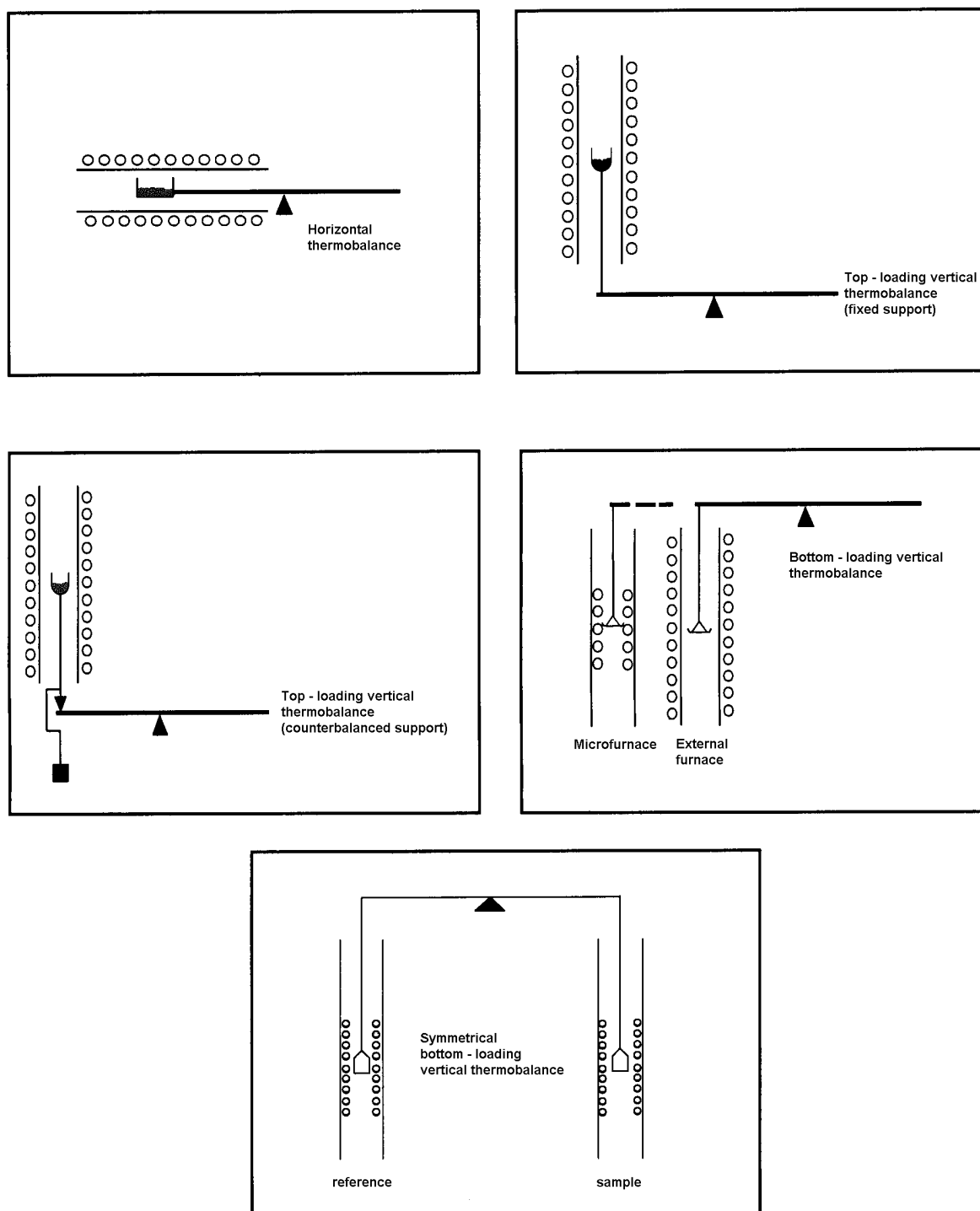reference   sample

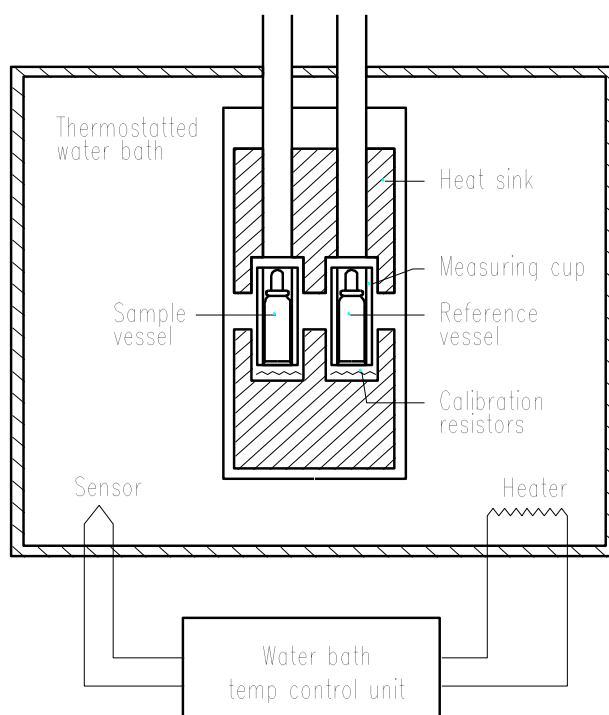Figure E-3: Schematic diagram of TGA apparatus

E-3

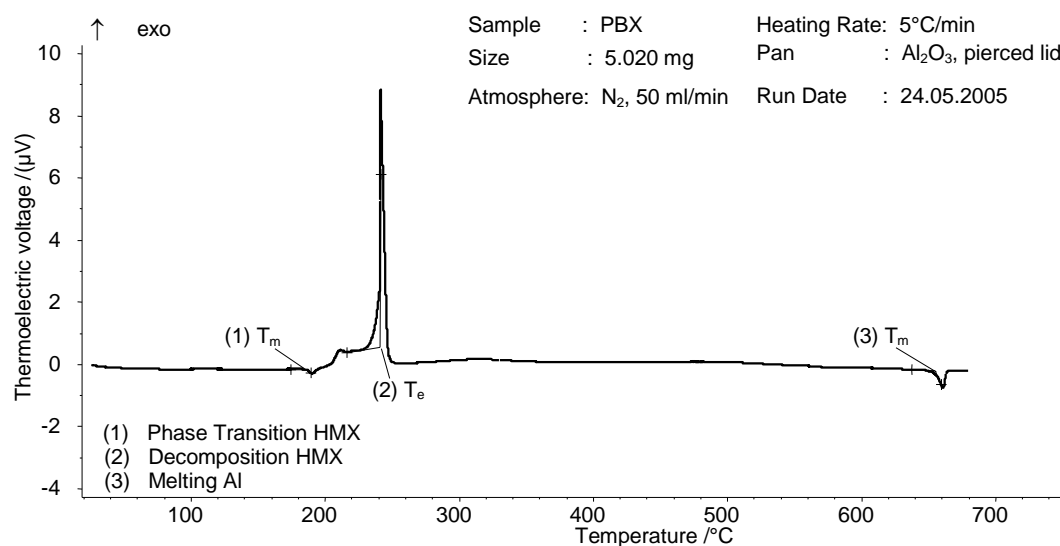Figure E-4. Schematic diagram of a heat flow calorimeter

EXAMPLES OF THERMAL CURVES

Figure F-1. Typical DTA curve

Figure F-2. Typical DSC curve

Sample   : AgN$_3$ Heating Rate: 0.5 °C/min

Size   : 1.616   Pan   : Al$_2$O$_3$, open

Atmosphere: Air, 10 ml/min   Run Date   : 04.01.2006
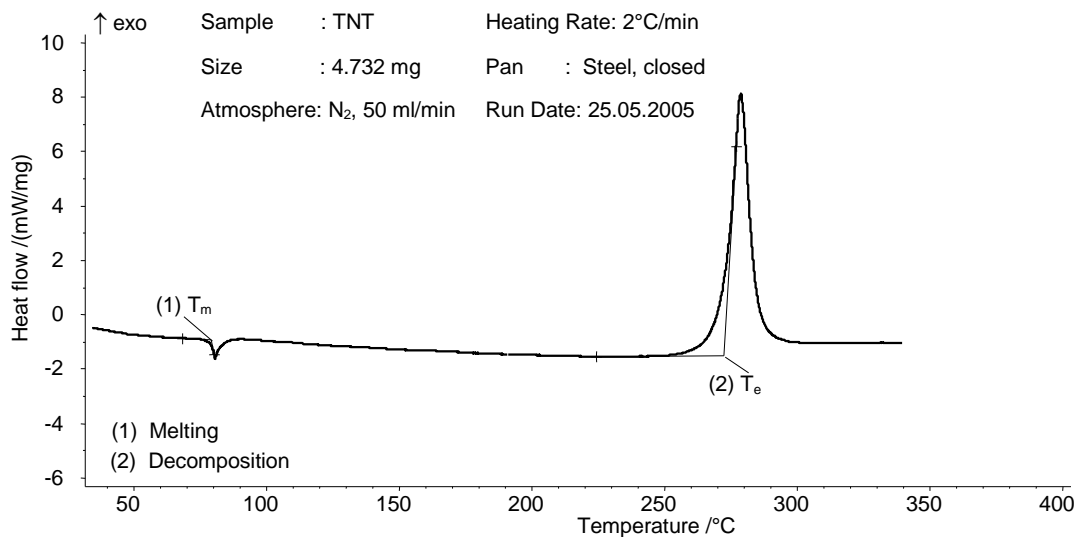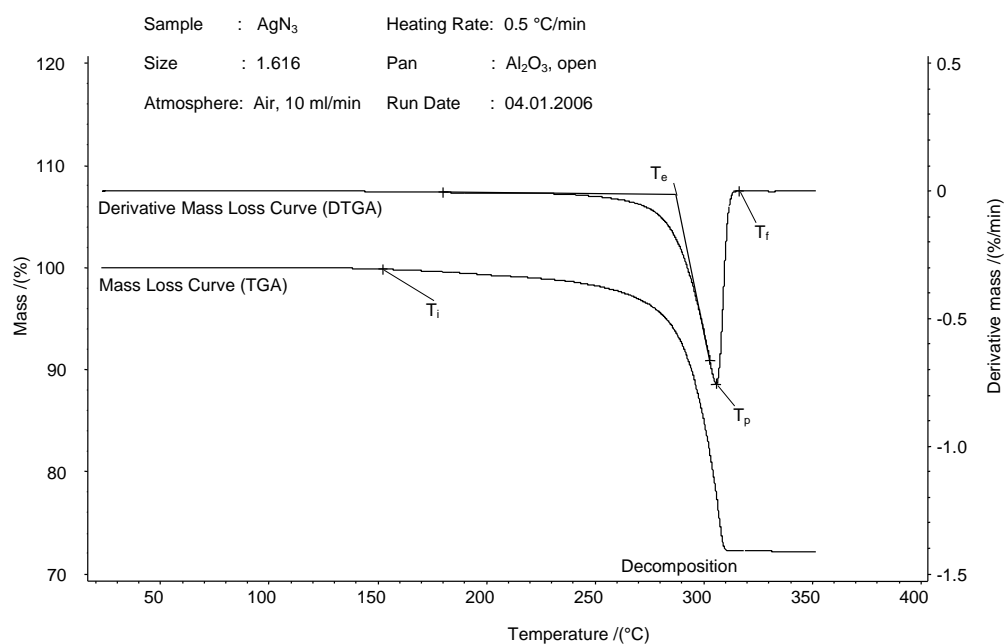

Figure F-3. Typical TGA and DTGA curves

Sample: DB propellant
Size: 3 g
Temperature: 89°C

P, µW/g
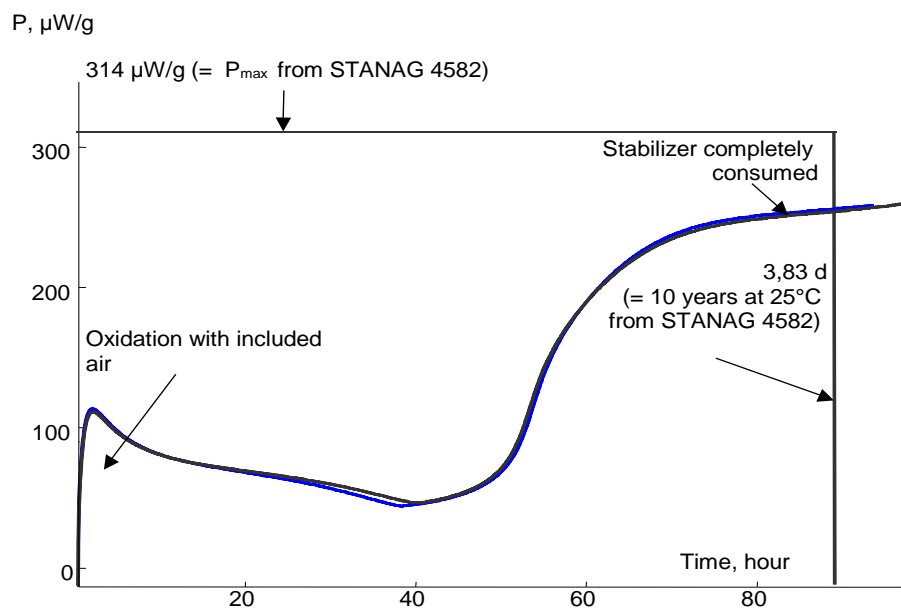

Figure F-4. Typical heat flow calorimetric measurement

REFERENCE MATERIALS FOR DSC AND DTA ANALYSIS

Table G-1. Reference Materials for Differential Scanning Calorimetry and Differential Thermal Analysis (the most commonly used materials are written in **bold**)

Substance	Transition	T_{tr} [K]	T_{tr} [°C]	$\Delta_{tr}H$ [J/g]	Remarks	Reference
2-Methylbutane	melting	113.37	-159.78	71.3	a	3
Cyclopentane	sol-sol	122.38	-150.77	69.60	a	1
2-Methyl-1,3-butadiene	melting	127.27	-145.88	71.7	a	3
Cyclopentane	sol-sol	138.06	-135.09	4.91	a	1
2,2-Dimethylpropane	sol-sol	140.51	-132.64	36.5	a	3
Pentane	melting	143.48	-129.67	116.5	a	3
2,2,3-trimethylpentane	melting	165.80	-107.35	80.6	a	3
Cyclopentane	melting	179.72	-93.43	8.63	a	1
Heptane	melting	182.60	-90.55	140.0	a	3
Cyclohexane	sol-sol	186.25	-86.90	79.8	a	3
1,3-Difluorobenzene	sol-sol	187.3	-85.9	7.3	a	3
1,3-Difluorobenzene	melting	204.08	-69.07	75.2	a	3
Mercury	**melting**	**234.32**	**-38.83**	**11.4**	**c**	**3**
2,2-Dimethylpropane	melting	256.76	-16.39	42.9	a	3
Water	**melting**	**273.15**	**0.00**	**333.6**		**2**
Hexafluorobenzene	melting	278.30	5.15	62.3		3
Cyclohexane	melting	279.81	6.66	31.5	a	3
Diphenylether	melting	300.01	26.86	107.1	a	3
Gallium	**melting**	**302.91**	**29.76**	**79.88**	**c**	**1, 3**
Biphenyl	melting	342.08	68.93	120.4	a	3
Naphthalene	melting	353.35	80.20	148.7	a	3
Benzil	melting	367.97	94.82	112.0	a	3
Acetanilide	melting	387.48	114.33	160.2	a	3
Benzoic acid	meting	395.50	122.35	147.9		3
Diphenylacetic acid	melting	420.41	147.26	147.3	a	3
Indium	**melting**	**429.75**	**156.60**	**28.62**	**c**	**1, 3**
Triphenylene	melting	471.02	197.87	108.4	a	3
Hexachlorobenzene	melting	501.83	228.68	87.6	a	3
Tin	**melting**	**505.08**	**231.93**	**60.40**	**c**	**1, 3**
Bismuth	**melting**	**544.55**	**271.40**	**53.83**		**1, 3**
Perylene	melting	551.25	278.10	126.3	a	3
Sodium nitrate	sol-sol	549	276	40.1		3
Sodium nitrate	melting	580	307	178.0		3
Lead	**melting**	**600.61**	**327.46**	**23.1**		**2**
Zinc	**melting**	**692.68**	**419.53**	**107.4**	**c**	**3**
Lithium sulfate	sol-sol	851.43	578.28	228.1	b	1, 3
Aluminium	**melting**	**933.47**	**660.32**	**398.1**	**c**	**1, 3**
Silver	**melting**	**1234.93**	**961.78**	**102.8**	**c**	**2**
Gold	**melting**	**1337.33**	**1064.18**	**-**	**c**	**2**

Remarks

a. Use hermetically sealed crucibles.

b. Use lithium sulfate mono hydrate in crucible that is not hermetically sealed; dehydration starts at about 110°C; beware of violent agitation of particles in the crucible during dehydration. Accurately measure sample mass after the measurement.

c. Fixed point material of the ITS-90 (International Temperature Scale of 1990).

References

1. S.M. Sarge, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Hemminger and W. Eysel, *The caloric calibration of scanning calorimeters*, Thermochim. Acta, 247 (**1994**) 129-168.

2. H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, G.W.H. Höhne and S.M. Sarge, *The temperature calibration of scanning calorimeters. Part 2. Calibration substances*, Thermochim. Acta, 219 (**1993**) 333-342.

3. R. Sabbah, A. Xu-wu, J.S. Chickos, M.L. Planas Leitão, M.V. Roux and L.A. Torres, *Reference materials for calorimetry and differential thermal analysis*, Thermochim. Acta, 331 (**1999**) 93-204.